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Survey of the Role of NO_x in Nonurban Ozone Formation

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Survey of the Role of NO_x in Nonurban Ozone Formation

by

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Research Triangle Park, North Carolina 27711

September 1979

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ABSTRACT

This study surveys and summarizes current knowledge about the role of oxides of nitrogen (NO_x) in the formation of ozone (O_3) in nonurban areas. Project elements include a literature review, a survey of expert opinion, and analyses of field data. The investigation was motivated by the U.S. Environmental Protection Agency's concern about the hypothesis that increased urban NO_x emissions could lead to higher levels of nonurban O_3.

The results of the study show that present knowledge about NO_x/O_3 interactions in nonubran areas is fragmentary, and that there is no direct quantitative description of the link between urban NO_x and nonurban O_3. Previous investigations suggest that increases in NO_x can enhance nonurban O_3, and that the impact of NO_x will vary with geographical location.

A preliminary analysis of nine rural and suburban sites indicates that transport is the principle mechanism associated with ozone levels that exceed 100 ppb. The analysis further suggests that transport times of the order of six to eight hours are most likely to be associated with the high ozone observed at these sites. A tenth rural site analyzed, located in Jetmore, Kansas, displayed a low level of local photochemical activity apparently because of a deficiency of hydrocarbons. Thus, increasing NO_x at this location is unlikely to lead to higher ozone.

Several areas requiring further research were identified. Three recommended research approaches aimed at elucidating the relationship between NO_x and nonurban O_3 are described; two are retrospective analyses of data, and one requires both data collection and analysis.

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I INTRODUCTION

This report describes the results of a study of the role played by nitrogen oxides (NO_x) in the formation of ozone (O_3) in nonurban areas. The investigation was performed in support of the U.S. Environmental Protection Agency's review of current strategies for controlling photochemical oxidant pollution.

A. Background

The recognition that the occurrence of elevated O_3 concentrations is a phenomenon that extends beyond the boundaries of urban areas has introduced additional complications into the already complex problem of how best to control photochemical oxidant pollution. Ozone being a secondary pollutant chemically synthesized in the troposphere from hydrocarbons (HC) and NO_x,* its control allows for various options regarding relative reductions in emissions of HC and NO_x. Current strategies emphasize reducing HC more than NO_x emissions, which results in low HC/NO_x ratios. Such a scheme is urban-oriented because it tends to slow down ozone formation near the emissions source. While this may be satisfactory for urban areas, it appears that this approach could worsen ozone pollution farther downwind, thereby shifting the air quality problems from one area to another. This possibility has prompted a reexamination of abatement policies, including the determination of whether more stringent NO_x controls are required.

Thus, from a regulatory standpoint, the question of interest is to determine the extent to which anthropogenic NO_x affects ozone formation outside urban areas. A primary purpose of this study is to review available evidence that may help define the nature of NO_x/O_3

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*Tropospheric ozone levels are also affected by injection of ozone from the stratosphere. In this report we are solely concerned with the formation of ozone from its precursors.

interactions in nonurban areas. However, the investigation is not intended to provide a definitive answer to the question.

B. Objectives and Methodology

The specific objectives of the project are to:

- Survey and summarize current knowledge about NO_x and its role in O_3 formation outside urban areas.
- Identify knowledge and data gaps where further research is indicated.
- Recommend research approaches that will help to define the relationship between NO_x and nonurban O_3.

To achieve the objectives, the scope of work of the project specified conducting a survey of the expert opinion of several leading researchers in the field. This was expanded to include performing an extensive review of the literature and a preliminary analysis of two new sources of data on nonurban NO_x and O_3. One source of measurements was the Sulfate Regional Experiment (SURE), which was sponsored by the Electric Power Research Institute. The other data source was a project conducted by SRI International in Jetmore, Kansas, which was sponsored by the Coordinating Research Council, Inc.

C. Report Organization

The literature review is described in Section II, and the results of the survey of expert opinion are summarized in Section III. Sections IV and V contain the analyses of field data. This is followed by conclusions and recommendations in Sections VI and VII, respectively. An extensive bibliography is provided in Section VIII.

II LITERATURE REVIEW

A. Introduction

The literature review was undertaken to survey current knowledge regarding the role of NO_x in nonurban ozone formation. The recent literature was surveyed extensively, including papers from scientific journals and technical reports published by public and private concerns. (Section VIII provides a complete bibliography.) The information gained was categorized under the following topic headings, each discussed in greater detail in the subsections that follow:

- NO_x Measurement Methods
- Nonurban NO_x Concentrations
- NO_x Sinks
- Sources of Nonurban NO_x
- NO_x Chemistry
- Mathematical Models
- NO_x/O_3 Relationship.

B. NO_x Measurement Methods

A number of methods have been used to measure oxides of nitrogen in the ambient atmosphere; manual and automated continuous methods are summarized in Table 1. Currently, the most commonly used method employs instruments based on the principle of chemiluminescence, which measures NO directly with high sensitivity and reliability. The chemiluminescent reaction

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + h\nu$$

Table 1

SUMMARY OF MEASUREMENT METHODS FOR NO_x IN AMBIENT AIR

(Knelson and Lee, 1977)

Method	Type	Description	Comments
Jacobs-Hochheiser	Manual	Collection in aqueous NaOH, conversion of NO_2 to nitrate ion, which is measured colorimetrically	Poor removal efficiency (35%); lack of constancy in correction factor; dropped as EPA reference method
Sodium arsenite	Manual	Similar to Jacobs-Hochheiser method; sodium arsenite added to aqueous NaOH collection solution	Collection efficiency improved to 85%
Triethanolamine	Manual	Collection in aqueous solution of triethanolamine containing small amount of organic compounds; colorimetric determination of nitrate ion	Appears to be reliable
Griess-Saltzman	Manual/ automated	Diazonium salf formed from the reaction of NO_2 with sulfanilic acid is coupled with N- (1-naphthol) -ethylenediamine dihydrochloride which is measured colorimetrically	Minimal interferences
Chemiluminescent	Automated	NO_2 quantitatively reduced to NO, which reacts with ozone to produce light	Measures NO and NO_x, not subject to interferences from common air pollutants, exhibits good precision

produces radiation emission in the 600 to 3000 nm range with a maximum at about 1200 nm. A photomultiplier tube is used to detect the luminescent radiation and thus the presence of NO.

Since only NO is measured directly, NO_x must be reduced to NO to allow for the measurement of NO_x ($NO + NO_2$). Although NO_2 has been converted to NO in many ways, most commercial instruments reduce NO_2 to NO catalytically at temperatures below 300°C. It is generally assumed that converter efficiency approaches unity. NO_2 has also been converted to NO at much higher temperatures (600°C), but this sometimes results in reduction to NO of several other interfering species, including ammonia (NH_3). The lower temperature ($< 300°C$) conversion of NO_2 to NO is therefore preferred.

Instruments that use converters below 300°C do not show interference from O_3, CO, NH_3, and SO_2. When present in high concentrations, peroxyacetyl nitrates (PANs) and organic nitrite may pose some interference problems. Depending upon the number of reaction cells, NO and NO_x can be measured either cyclically or simultaneously. The simultaneous measurement of NO and NO_x requires a dual reaction chamber and is particularly useful for aircraft operation.

Most commercially available chemiluminescent analyzers provide a sensitivity of 10 to 1000 ppb. A sensitivity of 10 ppb is generally unsatisfactory in most nonurban locations. Special instruments with a claimed full-scale range of 0 to 20 ppb, currently available, are more appropriate to the nonurban environment, where NO_x abundances of less than 5 ppb are commonly encountered and can be measured by these instruments with limited reliability. Modifications based on the chemiluminescent principle have been made to obtain a 0.01-ppb detection limit for NO (Drummond, 1977).* Such sensitivity becomes necessary in very clean environments approaching background levels of NO_x. Thus, for measurements in rural areas, chemiluminescent analyzers offer the best option. Slight interferences from PAN, HCl, and HNO_2 may exist, but are unlikely to be important in rural environments. Calibrations for NO can be performed using multiple-dilution techniques and the standards can be stored for a relatively long period of time. NO_2 calibrations can either be done from NO standards by gas phase titration or by using permeation tubes. Commercial instrumentation can be modified to achieve better sensitivities with only limited reliability below 1 ppb for NO.

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*References are listed at the end of the report.

A column content measurement of tropospheric NO_2 has been made by Noxon (1975, 1978) using absorption spectroscopy. The identification of NO_2 with complete spectral scans at 5°A interval between 4350 to 4500°A was considered to be unambiguous. The method can be used to make NO_2 column content measurements in the atmosphere using the sun as the source. This method was one of the first to suggest tropospheric NO_2 levels of less than 0.1 ppb, a concentration that is beyond the capability of most chemiluminescent analyzers. The method is most suitable for obtaining spatial averages (rather than point estimates) of concentration, and is still in a developmental stage.

C. Levels of Nonurban NO_x

To understand the nonurban NO_x phenomenon it is necessary to examine the concentrations of NO_x observed at a variety of locations ranging from clean remote areas to suburban locales directly impacted by emissions from neighboring cities.

Below we discuss NO_x measurements that have been reported in the literature. We also include measurements for urban areas to span the full range of NO_x concentrations. In Sections IV and V of this report we supplement the figures obtained from the literature with data collected in 1977 at several nonurban locations in the United States.

Tables 2 through 4 catalog NO_x concentrations observed in remote, rural and suburban, and urban areas, respectively. In addition to the NO_x levels, the tables show the location, method, and date of the

Table 2

CONCENTRATION OF NITROGEN OXIDES OBSERVED IN CLEAN REMOTE AREAS

Location	Concentration (ppb)			Measurement Method	Date of Measurement	Reference	Remarks
	NO_x	NO	NO_2				
Laramie, Wyoming	0.1 - 0.4	0.01 - 0.05		Chemiluminescent	Summer 1975	Drummond (1977)	
Fritz Peak, Colorado			<0.1	Absorption spectroscopy	Fall 1974; Summer-Spring, 1975-1976	Noxon (1975, 1978)	
Fritz Peak, Colorado	0.2 - 0.5			Chemiluminescent	Sep 1977	Ritter et al. (1978)	
Northern Michigan	0.3 - 0.5			Chemiluminescent	Jun 1977	Ritter et al. (1978)	10-day average
Tropical Areas		0.1 - 0.5	0.2 - 0.4	Saltzman	1965-1966	Lodge and Pate (1966); Lodge et al. (1974)	Under forest canopy
		0.3 - 0.4	0.3 - 0.5			Lodge and Pate (1966); Lodge et al. (1974)	Above forest canopy
		0.3 - 0.7	0.3 - 0.6			Lodge and Pate (1966); Lodge et al. (1974)	River bank
		0.3 - 0.7	0.3 - 0.5			Lodge and Pate (1966); Lodge et al. (1974)	Seashore and maritime
Ireland		≤0.2	0.2 - 1.5	Chemiluminescent	Jul-Nov 1974	Cox (1977)	Maritime. Maximum hourly averages ranged from 0.3 to 5.0 ppb.

Table 3

CONCENTRATION OF NITROGEN OXIDES OBSERVED IN RURAL AND SUBURBAN AREAS*

Location	Concentration (ppb)			Measurement Method	Date of Measurement	Reference	Remarks
	NO_x	NO	NO_2				
Piedmont, North Carolina		1.9	5.6	Modified Saltzman	Nov 1965-Jan 1966	Ripperton et al. (1970)	
Porton, England			10	Modified Saltzman	Oct 1972-Jan 1973	Nash (1974)	Mean of 13 samples. Range is 4-21 ppb.
Athensville, Illinois and Cofman, Missouri			1-3	Saltzman	Oct-Nov 1971	Breeding et al. (1973)	
Wilmington, Ohio			7	Chemiluminescent	Jun-Aug 1974	†	Mean hourly concentration obtained from continuous samples
McConnelsville, Ohio			6	Chemiluminescent	Jun-Aug 1974	†	
Wooster, Ohio			7	Chemiluminescent	Jun-Aug 1974	†	
McHenry, Maryland			6	Chemiluminescent	Jun-Aug 1974	†	
DuBois, Pennsylvania			10	Chemiluminescent	Jun-Aug 1974	†	
Fritz Peak, Colorado			10	Absorption spectroxcopy	Fall 1974	Noxon (1975)	Column average concentration is attributed to transport from Denver
New Carlisle, Ohio	17	5		Chemiluminescent	Jul-Aug 1974	Spicer et al. (1976a)	Twenty-day average from continuous samples
Huber Heights, Ohio	26	8		Chemiluminescent	Jul-Aug 1974	Spicer et al. (1976a)	Suburban location
Cold Lake, Alberta, Canada			1-2	Absorption spectroscopy	Feb 1977	Noxon (1978)	Column average
Bradford, Pennsylvania		2	2.7	Chemiluminescent	Jun-Sep 1975	†	
Creston, Iowa		3.8	2.3	Chemiluminescent	Jun-Sep 1975	†	
Wolf Point, Minnesota		<1	<1	Chemiluminescent	Jun-Sep 1975	†	
De Ridder, Louisiana		1.5	2.6	Chemiluminescent	Jun-Sep 1975	†	

*All locations are rural unless otherwise specified.

†Research Triangle Institute (1976).

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Table 4

CONCENTRATION OF NITROGEN OXIDES OBSERVED IN URBAN AREAS

Location	Concentration (ppb)			Measurement Method	Date of Measurement	Reference	Remarks
	NO_x	NO	NO_2				
San Francisco Bay Area, California			22 - 42	Chemiluminescent and modified Saltzman	1977	California Air Resources Board (1978)	Range of annual average NO_2 for the area. Range of maximum hourly average NO_2 is 110-260 ppb.
Los Angeles County, California			35 - 89	Chemiluminescent and modified Saltzman	1977	California Air Resources Board (1978)	Range of annual average for the area. Maximum hourly averages ranged from 240 to 690 ppb.
Boulder, Colorado			<0.5 - 20	Absorption spectroscopy	Feb 1977	Noxon (1978)	Column average
Denver, Colorado			1 - 40	Absorption spectroscopy	Feb 1977	Noxon (1978)	Column average
Edmonton, Alberta, Canada			4 - 20	Absorption spectroscopy	Feb 1977	Noxon (1978)	Column average
Dayton, Ohio	47	22		Chemiluminescent	Jul-Aug 1974	Spicer et al. (1976a)	20-day average. Range of maximum hourly averages is 40-451 ppb for NO_x and 12 to 408 ppb for NO.

measurements, as well as the corresponding literature reference. Unless otherwise specified, all measurements were made at ground level. In compiling these tables we have purposely omitted any measurements obtained using the Jacobs-Hochheiser method, in view of the well-known problems associated with this procedure (Federal Register, 1973; cf. Table 1).

Several aspects of the tables require explanation. The first concerns the concentration estimates obtained using absorption spectroscopy. These concentrations are averages taken over a column of air whose horizontal and vertical dimensions are of the order of a few kilometers. Hence, this method smooths out concentration gradients and in general will yield pollutant estimates that are lower than ground-level measurements. These considerations are important in urban areas, where gradients can be steep; they are of less consequence in cleaner environments, where uniformity is the rule.

Second, the tables give average values of the compounds, when available, in order to portray long term conditions at the various sites.

The third and final point entails distinguishing between remote, rural, and suburban sites. A remote location is one that is far from populated areas; hence, its pollutant levels are seldom influenced by anthropogenic sources. However, in the United States, even remote areas are sometimes affected by pollutants transported from urban areas, as evidenced by the entries for Fritz Peak, Colorado, in Tables 2 and 3. A rural site, by contrast, would be one that is more likely to be impacted by transport from urban areas. Rural sites include small communities that generate pollutants, but in general do not contain any major sources of pollution. Suburban areas are those that are within commuting distance, (viz., 20 to 25 miles) of an urban area, and thus bear the brunt of transport from the urban core.

Examination of Tables 2 through 4 reveals certain patterns of NO_x levels for the various areas. Table 2 shows that remote sites have NO_x concentrations that are below 1 ppb. Chemiluminescent measurements show NO_x ranging from 0.1 to 0.5 ppb, the bulk of the NO_x being NO_2, whereas the absorption spectroscopy method suggests that NO_2 is less than 0.1 ppb. The latter figure has been questioned by Ritter et al. (1978), whose concurrent ground-level chemiluminescent measurements of NO_2 at Fritz Peak found higher concentrations. The discrepancy probably results from the estimation procedure used to obtain the volumetric column average from the molecular density measurements obtained by absorption spectroscopy. The procedure requires assuming an effective height for the mixed layer, a quantity that is subject to large uncertainties. Because no such assumption is involved in Ritter's concentration estimate, we believe it to be the more accurate.

Measurements of NO at remote sites are very sparse, the most reliable being those by Drummond (1977); they suggest a mean NO/NO_x ratio of less than 0.2. The same bound is indicated by data collected by Ritter et al. (1978) under clean conditions at a site in Michigan. Thus, it appears that, on the average, NO_2 is the predominant species in remote locations. However, either NO or NO_2 can predominate at any given instant. As a footnote, it is noted that the values of NO_2 shown in Table 2 for maritime sites generally agree with the 0.5 ppb ocean background level suggested by Robinson and Robbins (1970).

For rural areas, Table 3 shows that mean NO_2 concentrations range from 1 to 10 ppb. The data for the single suburban site at Huber Heights, Ohio, suggests an NO_2 level in excess of 10 ppb. Although reported NO measurements are scarce, the available data indicate NO/NO_x ratios greater than 0.2. This was expected, since these sites are likely to be influenced by sources such as roads, urban areas, and power plants whose respective plumes can contain substantial amounts of unreacted NO.

As shown in Table 4, urban areas contain a wide range of NO_2 values, the means ranging from 1 to 90 ppb, with peak hourly levels exceeding 600 ppb in Los Angeles. The NO/NO_x ratio for Dayton is about 0.5, which should be typical of urban areas. Of course, morning (0600-0900 LT) levels of NO_x in cities are primarily attributable to mobile sources, and NO is the predominant compound by far in this time interval.

To summarize, the data obtained from the literature indicate NO_x levels below 1 ppb in remote areas, with a mean NO/NO_x ratio bounded above by 0.2. For rural areas, mean NO_x levels range from 1 to 10 ppb, with an NO/NO_x ratio of 0.2 or greater In urban areas, mean NO_2 levels span the range 1 to 100 ppb, the concentrations varying widely depending on geographical location. The mean NO/NO_x ratio in urban areas probably exceeds 0.5.

Regarding NO_2 background levels, it should be noted that the 4 ppb concentration proposed by Robinson and Robbins (1970) as a "natural background" level for land areas in northern temperate zones is within the range of cooncentrations observed in rural areas of the United States. However, recent NO_2 measurements at remote locations show NO_2 being less than 1 ppb, which suggests that the 4-ppb level contains a sizable anthropogenic component. This implies that previous estimates of the atmospheric residence time of NO_2 need to be reevaluated.

D. Sinks of NO_x

Once in the atmosphere, NO_x ($NO + NO_2$) is subject to various removal processes. Atmospheric residence times from 1 to 20 days have been suggested. Two principal removal mechanisms are operational:

- Direct removal of gaseous NO_x by dry and wet deposition processes.
- Conversion of NO_x to nitric acid or particulate nitrate, followed by removal by dry or wet deposition processes.

In the atmosphere, NO_2 is oxidized to nitric acid, nitric acid aerosols, and nitrate aerosols via several pathways listed in Table 5. The quantitative importance of the mechanisms listed in Table 5 is currently uncertain. In the relatively clean atmosphere, at least half of the NO_2 is converted to HNO_3 via reaction with HO. The second path (Reactions 2 through 4), involving conversion of NO_2 to NO_3, N_2O_5, and finally HNO_3, would be about a third as fast as the reaction with HO in rural atmospheres. It is quite possible, however, that Reactions 2, 3, and 4 may dominate in polluted atmospheres with very high ozone levels.

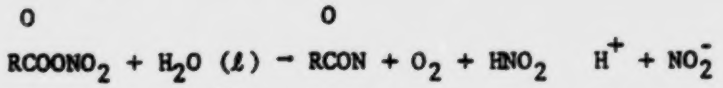
The volatility of nitric acid is such that it is not appreciably taken into water droplets unless the droplets contain neutralizing reactants. It would thus appear that homogeneous nucleation (Reactions 5 through 7) would not constitute an important mechanism for nitrate formation.

Nitric acid can exist in the gas phase or react with ammonia to form particulate ammonium nitrate. It has also been postulated that aerosol formation could result from direct absorption of NO_x into aqueous droplets in the presence of ambient ammonia (Paths III and IV). While both processes may proceed simultaneously, the presence of ammonia seems to be essential. The atmospheric abundance of ammonia in urban and rural atmospheres is poorly determined. Moreover, the rate constants (especially that for Reaction 7) are not firmly established. Thus, while Paths III and IV may be important, it is not possible to obtain a quantitative estimate of their contribution. It is predicted that about half of NO_x is converted to nitric acid and nitrates before being lost. Nitric acid may be an important component of acid rain.

In the lower atmosphere, and where some pollution exists, other sinks may be possible. For example, NO_x in the presence of organics is converted to organic nitrogen compounds (such as peroxyacetyl nitrates, PANs) that could then be lost to the ground by dry or wet deposition or could slowly hydrolyze (Path V). While present in the gas phase, PANs may not be a final sink for NO_x, since they may decompose to regenerate

Table 5

NITRIC ACID AND NITRATE AEROSOL FORMATION REACTIONS

Path	Reaction No.
I Nitrogen dioxide - hydroxyl radical reaction:	
$NO_2 + HO^{\cdot} + M \rightarrow HNO_3 + M$	1
II Nitric acid anhydride reaction:	
$NO_2 + O_3 \rightarrow NO_3 + O_2$	2
$NO_3 + NO_2 \rightarrow N_2O_5$	3
$N_2O_5 + H_2O \rightarrow 2HNO_3$	4
III Homogeneous conversions of nitric acid to aerosol:	
HNO_3 (g) + H_2O (g) → HNO_3 aerosol	5
N_2O_5 (g) + H_2O (ℓ) → HNO_3 aerosol	6
NH_3 (g) + HNO_3 (g) → NH_4NO_3 aerosol	7
IV NO_x absorption into aerosol droplets:	
$2NO_2 + H_2O$ (ℓ) → $HNO_3 + HNO_2$ (aqueous solution)	8
$NO + NO_2 + H_2O$ (ℓ) → $2HNO_2$ (aqueous solution)	9
HNO_2 (aq.) → $H + NO_2^-$ (aqueous solution)	10
$NO_2^- + \frac{1}{2}O_2$ (in aerosol solution) → NO_3^-	11
$NO_2^- + O_3$ (in aerosol solution) → $NO_3^- + O_2$	12
V Hydrolysis of PANs:	
 $\overset{O}{RCOONO_2} + H_2O (\ell) \rightarrow \overset{O}{RCON} + O_2 + HNO_2 \quad H^+ + NO_2^-$	13
$NO_2 + O_2 \rightarrow NO_3^-$	14
VI Methyl nitrate formation:	
$CH_3O^{\cdot} + NO_2 \rightarrow CH_3NO_3$ Methoxy radical — methyl nitrate	15
VII Pernitric acid formation:	
$HO_2 + NO_2 \rightarrow HO_2NO_2$	16

NO_2 and organic radicals. The formation of methyl nitrate has also been postulated, although no conclusive atmospheric identification has been made. Its atmospheric fate is largely unknown; however, reaction with HO is expected to provide at least one removal mechanism. Another temporary sink could be pernitric acid (HO_2NO_2), but it is likely to be important only at relatively colder temperatures. At temperatures greater than 70°F, when most smog occurs, the role of HO_2NO_2 is limited (Cox et al., 1977).

Gaseous nitrogen species may be used up by surface absorption. Vegetation and soil are capable of removing significant amounts of NO, NO_2, PAN, and other species from the atmosphere (Tingey, 1968; Rogers et al., 1977; Hill, 1971; Sundareson et al., 1967). Dry deposition of particulate matter occurs through sedimentation, Brownian motion, and impaction. Dry deposition of gaseous NO_x is only about half as effective as the corresponding particulate dry deposition. The rate of removal is strongly dependent on wind speed and the nature of the deposition surface.

Rainout and washout are the two major wet removal processes. The former refers to the processes of nucleation occurring within a cloud; the latter involves removal below the clouds by falling hydrometeors. Due to high concentration of nitrogen species within the boundary layer, washout may dominate the removal process. In the free troposphere, however, both processes may play an important role. Together, wet and dry deposition are the major ultimate sinks for the nitrogen containing species.

E. Chemistry of NO_x

Nitrogen oxides play a principal role in smog formation. Perhaps the most central reaction is the NO-NO_2 null cycle:

$$NO_2 + h\nu(385\ \text{rm} < \lambda < 435\ \text{nm}) \rightarrow NO + O \quad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (2)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (3)$$

NET: no reaction

The NO-NO_2 null reaction becomes important when the system is perturbed by the inclusion of hydrocarbons. In a complex way, the hydrocarbons induce the oxidation of NO to NO_2 without involving O_3 destruction. This is accomplished by the peroxy free radicals in Reaction 4, and results in net O_3 production as indicated below

$$RO_2 + NO \rightarrow RO + NO_2 \quad (4)$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

NET: $RO_2 + O_2 \rightarrow RO + O_3$

The peroxy free radicals are principally produced from hydrocarbon attack by free radicals [HO, $O(^3P)$] and by ozone itself. Of these HO is known to play a dominant role

$$RH + HO \rightarrow R + H_2O \qquad (5)$$

$$R + O_2 \rightarrow RO_2 \qquad (6)$$

where RH denotes a generic hydrocarbon compound.

Other peroxy free radicals, such as RCO_3, are also produced by reaction of HO with alhehydes and that of O_3 with olefins. The RO radicals generated in Reaction 4 are oxidized by oxygen to form aldehydes ($RO + O_2 \rightarrow HO_2$ + aldehydes). In a way similar to RO_2, the RCO_3 radical can also lead to net O_3 formation as follows:

$$\begin{array}{l} RCO_3 + NO + O_2 \rightarrow RO_2 + NO_2 + CO_2 \qquad (7) \\ NO_2 + h\nu \rightarrow NO + O \\ O + O_2 + M \rightarrow O_3 \\ \hline \text{NET:} \quad RCO_3 + 2O_2 \rightarrow RO_2 + O_3 + CO_2 \end{array}$$

Thus, the RCO_3 radical not only contributes to net O_3 production but also releases an RO_2 radical, which can continue the chain reactions. Thus, in principle, this chain will continue as long as there is NO_x, hydrocarbons, and sunlight. By allowing the oxidation of NO to NO_2 by processes other than reaction with O_3 (Reaction 3), a build-up of O_3 takes place. Almost any hydrocarbon (also CO) that can react with free radicals can participate in the ozone-forming process.

While initially the reactive free radical HO is released from O_3 photolysis, eventually other reactions take over as follows:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{8a}$$

$$O(^1D) + H_2O \rightarrow 2HO \tag{8b}$$

$$HO_2 + NO \rightarrow NO_2 + HO \tag{9}$$

In the very clean atmosphere, Reaction 8 is the dominant source of HO, whereas in a highly polluted atmosphere Reaction 9 predominates. In rural atmospheres, it is possible that both reactions would be important contributors to ambient HO.

Perhaps the simplest smog cycle is due to CO:

$$\begin{array}{l}
CO + HO \rightarrow CO_2 + H \\
H + O_2 + M \rightarrow HO_2 + M \\
HO_2 + NO \rightarrow HO + NO_2 \\
NO_2 + h\nu \rightarrow NO + O \\
O + O_2 + M \rightarrow O_3 + M \\
\hline
\text{NET:}\quad CO + 2O_2 \rightarrow CO_2 + O_3
\end{array}$$

However, in suburban and rural areas, where CO levels are low, the CO-related reactions are generally not significant ozone producers. In remote areas and in the free troposphere, it is hypothesized that CO could become important in the presence of NO_x levels greater than 0.1 ppb.

The chain-carrying radicals are also destroyed in a number of ways. In some cases, the radicals provide a sink for NO_x. Important chain-termination reactions are as follows:

$$HO + NO_2 + M \rightarrow HNO_3 + M$$

$$HO + HO_2 \rightarrow H_2O + O_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$RCO_3 + NO_2 \rightleftarrows RCO_3NO_2 \text{ (PAN)}$$

$$NO + NO_2 + H_2O \rightarrow 2HNO_2$$

$$HNO_2 + h\nu \rightarrow HO + NO$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \rightarrow N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

$$HO_2 + NO_2 \overset{M}{\rightleftarrows} HO_2NO_2$$

$$HO_2 + NO_2 \rightarrow HONO + O_2$$

It should be noted that the ratio of the rates of forward and reverse reactions for PAN and HO_2NO_2 is highly-temperature dependent, the rate of the reverse reaction increasing with temperature (Hendry and Kenley, 1978).

All mechanisms of ozone formation in the troposphere need NO_x for ozone synthesis. In the urban centers, NO_x may build to such high levels as to actually suppress O_3 production. This is unlikely to happen in nonurban locations where NO-NO_2 levels are relatively low. Since the rate of NO_x removal from the atmosphere is at least of the order of several hours, fresh emissions allow a residue of NO_x to remain that is sufficient to sustain the photochemical chain reactions that result in smog formation. It is also possible that O_3 gas phase loss mechanisms are minimized in nonurban areas and the smog cycle is more efficient. It is expected that hydrocarbons of either man-made or natural origin would be available in nonurban areas to participate in smog chemistry. In the free troposphere, the important carbon compounds would be CH_4, C_2H_6, and CO. In the nonurban atmosphere, other light alkanes would dominate (butanes, pentanes). Small amounts of alkenes, (e.g., C_2H_4) may also be present (Singh et al., 1978).

F. Sources of NO_x

Both man-made and natural sources contribute to the total atmospheric NO_x burden. The natural NO_x sources at this time are poorly understood and are largely speculative.

1. Man-Made Sources

The principal source of nitrogen oxides is the oxidation of atmospheric nitrogen in combustion processes. The oxidation of nitrogen at high temperatures primarily occurs through the following mechanisms:

$$O_2 \rightleftarrows 2O$$

$$O + N_2 \rightleftarrows NO + N$$

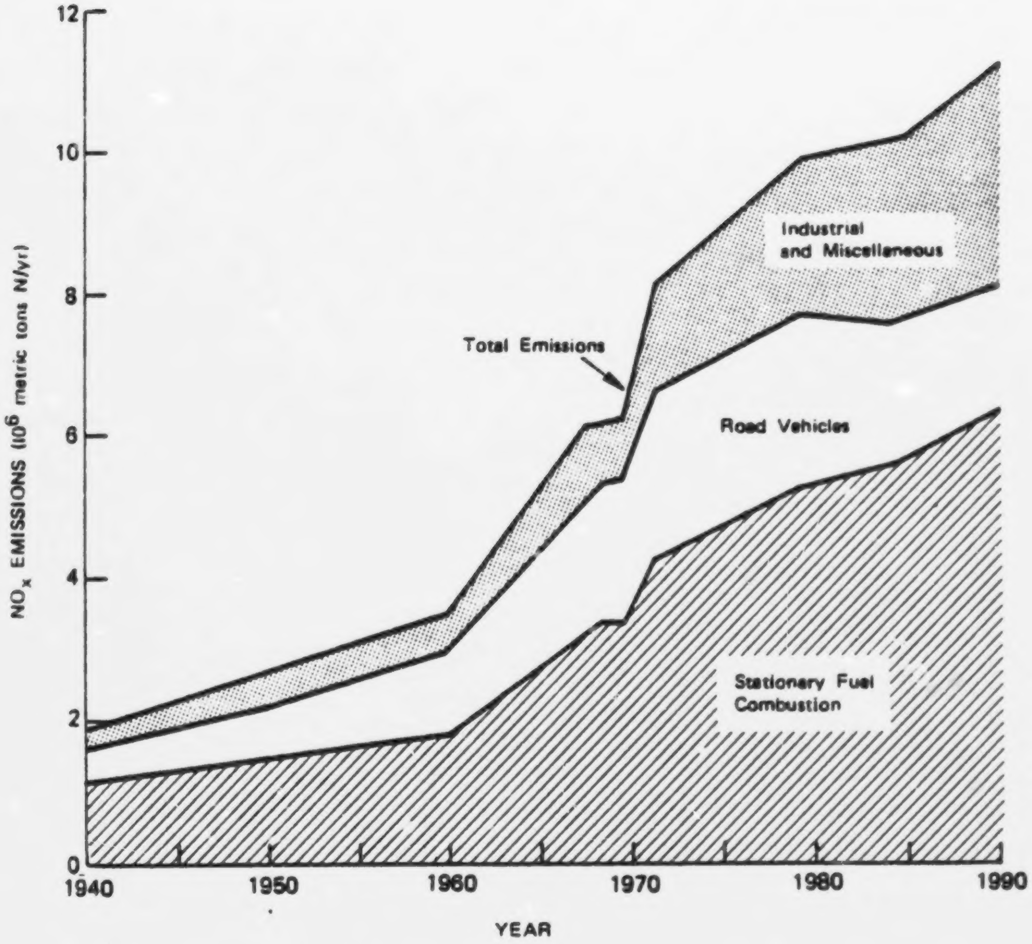
$$N + O_2 \rightleftarrows NO + O$$

The production of NO is critically dependent on the atomic oxygen concentration, which in turn is dependent on the combustion temperature. The most common combustion processes involve:

- Fuels--coal, petroleum, wood, natural gas, refuse
- Processes--power generation, industry, domestic heating, refinery production, transportation, controlled burning (forest, sugar cane), and incineration, among others.

Figure 1 shows the actual and projected trends in emissions of NO_x in the United States by source categories. The global man-made emissions have been estimated to be three times those of the United States (Soderlund and Svensson, 1976). Thus, it is possible to estimate that currently about 10 Mt(N)/yr of NO_x is emitted in the United States and the estimate of global emission rate is 30 Mt(N)/yr.

Not all NO_x is released in a primary mode. Combustion sources, animal wastes (feedlots and pastures), and volatilization of nitrogen fertilizer release significant quantities of ammonia, which can be oxidized to NO or NO_2 in the atmosphere. This conversion process is poorly understood, and its occurrence has been questioned (Cox et al., 1975a). No complete NH_3 emissions inventory is available for the United States. Best estimates are that man-made activities result in the release of 50 to 80 Mt(N)/yr of ammonia (National Academy of Sciences, 1978). Burning of coal accounts for 4 to 12 Mt, volatilization from animal and human waste account for 20 to 35 Mt, and inefficiencies in handling and application account for about 30 Mt of NH_3. Thus, in principle, man-made releases of ammonia can be larger than direct releases of NO_x. Best estimates are that no more than 3 to 4 percent of ammonia would be converted to NO_x (National Academy of Sciences, 1978). Thus, emissions of ammonia would contribute about 10 percent to the NO_x burden.



Source: National Academy of Sciences, 1978

FIGURE 1 ACTUAL AND PROJECTED TRENDS IN EMISSIONS OF NO_x IN THE UNITED STATES BY SOURCE CATEGORIES

2. Natural Sources

Natural sources also release NO_x and NH_3 via a variety of mechanisms. The quantitative estimates of fluxes are poorly understood, however. Table 6 shows the various natural processes that result in a release of either NO_x or NH_3.

Table 6

NATURAL SOURCES OF NO_x

Source Type	Major Species*
Soil: decomposition and volatilization of organic matter and animal wastes under alkaline conditions	NH_3
Chemodenitrification in acidic swamps and soils	NO
Forest fires	NH_3, NO_x
Volcanoes	NH_3, NO_x (?)
Lightning	NO_x
Inflow from the stratosphere (from photolysis of N_2O)	NO_x

*Since N_2O is unreactive in the troposphere, it is not included.

Of all the processes listed in Table 6, the biological and chemical transformations of nitrogen compounds in the soil appear to be an important source NO_x. Although this source is poorly quantified, a global flux of 3 to 60 Mt(N)/yr can be estimated (Ratsch and Tingey, 1978; Soderlund and Svensson, 1976). Inflow from the stratosphere (from N_2O decomposition and photolysis) is not expected to exceed 0.5 Mt(N)/yr and is negligibly small. Soderlund and Svensson (1976) estimate that an NO_x source of 20 to 90 Mt/yr is necessary to balance the NO_x cycle. The difference between the soil source and total NO_x required may be explained by NO_x generated from lightning. Estimates of global production by lightning range from 10 to 20 Mt(N)/yr (CAST, 1976; Delwiche, 1970; Holland, 1973). More recently, however, Chameides et al. (1977) estimate that global production of NO_x during lightning is 30 to 40 Mt/yr. Although uncertainties abound, it is possible that a global natural source of NO_x is 20 to 90 Mt(N)/yr and is largely composed of NO_x produced by lightning and biological and chemical transformations in the soil.

Emissions of NH_3, however, are expected to be much larger. Estimates of Robinson and Robbins (1971) suggested a natural NO_3 source of 870 Mt(N)/yr. Soderlund and Svensson (1976) have improved this estimate and suggest that the natural sources of NH_3 lie between 80 and 200 Mt/yr. The available data are extremely poor and subject to major revisions. Together, both natural and man-made sources of NH_3 would result in the formation of 2 to 8 Mt/yr of NO_x.

G. Mathematical Models

Efforts to model photochemical pollution date back to the late 1960s, their main thrust being the simulation of urban pollution. Urban-oriented models continue to be developed, improved, and refined; a useful summary of the state of the modeling art for urban areas circa 1976-1977 is given by Seinfeld and Wilson (1977). More recently, a number of models have been developed that attempt to describe nonurban pollution. The discussion that follows reviews these models. Because we are concerned with models that attempt to simulate the physical processes governing photochemical air pollution, our review will not include statistical or curve-fitting approaches to the estimation of pollutant levels.

The review will be concerned with the following aspects of the models:

- Model type
- Domain of applicability of the model
- Verification tests.

The first aspect, model type, encompasses the structure and contents of the model. The second aspect specifies those conditions under which the model can be applied. The last, verification tests, examines the extent to which the models have been tested against experimental data. Applications of the models will be discussed in the section that examines the relationship between NO_x and O_3 in nonurban areas.

1. Model Type and Intended Application

All the models reviewed fall into one of two categories:

- Those that have chemistry only

- Those that contain both chemistry and meteorology.

Some models operate under steady-state assumption , and others simulate time-dependent conditions. Table 7 lists and classifies the models reviewed; each model is identified by the name of the developer(s). The table also shows the type of application for which each model is intended.

The models listed in Table 7 have as their centerpiece a set of chemical reactions that describe the photochemistry of nitrogen oxides, ozone, and hydrocarbons. The kinetic modules of the various models are similar in many ways, which implies that there is general agreement on the major features of the chemistry. In particular, the description of the gas phase chemistry of NO_x differs only slightly in the various models. The major chemistry differences involve the hydrocarbons. Thus, models that simulate clean environments do not include the same hydrocarbons that appear in models intended for more polluted areas. In general, the models emphasize chemistry at the expense of transport and

Table 7

PHOTOCHEMICAL MODELS FOR NONURBAN AREAS

Model Identification	Classification*	Intended Application	References
Chang and Weinstock	Chemical; time-dependent	Rural areas influenced by urban transport	Chang and Weinstock (1967a,b)
Chameides	Steady-state; chemistry and parameterized vertical transport	Remote areas	Chameides (1978); Chameides and Stedman (1977)
Liu	Time-dependent; chemistry and parameterized vertical transport	Remote areas	Liu (1977); Liu et al. (1976)
Fishman and Crutzen	Time-dependent; chemistry and vertical transport and diffusion	Remote areas	Fishman and Crutzen (1977)
Hov and Isaksen	Time-dependent; chemistry and parameterized dilution	Rural areas influenced by urban transport	Isaksen et al. (1978a,b); Hov et al. (1978)
Graedel and Allara	Time-dependent; chemistry and instantaneous mixing within a variable volume	Rural areas influenced by urban transport	Graedel and Allara (1976)

*All the models are one-dimensional.

diffusion. Moreover, the models are one-dimensional, i.e., they consider a single column of air as it moves over a region.

Chang and Weinstock's model employs 57 reactions, including reactions for methane (CH_4), other alkanes, and aldehydes. The model assumes instantaneous mixing and considers the air column to be a moving reactor.

The models devised by Chameides and by Liu use the same chemical description, which contains 47 reactions. Being intended for simulating remote environments, the chemistry does not include aldehydes or any primary hydrocarbons other than CH_4. Thus, CH_4 oxidation is the principal source of organic radicals in these models. The two models differ only in the numerical values assigned to some of the reaction rate constants. Chameides' model assumes steady state conditions, and thus is useful only for estimating bounds on pollutant levels. Liu's model operates under dynamic conditions, thereby yielding concentration histories for the species of interest. Neither model can be used to assess the impact on ozone of hydrocarbons and NO_x transported from urban areas. It may be possible to study the effect of NO_x transport on NO_x and ozone levels using these models.

The meteorological component of Fishman and Crutzen's model is more elaborate and realistic than in the models previously discussed, since it includes time-dependent vertical diffusion and transport. Its chemical module contains 42 reactions and, as in the case of Chameides's and Liu's models, considers CH_4 oxidation to be the principal source of organic radicals. The model can be used in a qualitative sense to gain insights about the interactions of the various species.

The Hov and Isaksen model treats chemistry in great detail. Its chemical module contains 161 reactions for NO_x and seven hydrocarbons. The hydrocarbons are associated with urban plumes, and consist of propene (C_3H_6), ethylene (C_2H_4), m-xylene (mC_8H_{10}), acetylene (C_2H_2), n-butane (nC_4H_{10}), and n-hexane (nC_6H_{14}), as well as CH_4. The model assumes instantaneous vertical mixing within the mixed layer in a moving air column whose horizontal dimensions are assumed to be large enough to justify neglecting horizontal diffusion. However, the model allows the mixing volume to change with time.

Hov and Isaksen's model represents an ambitious attempt to simulate the phenomena associated with photochemical smog formation downwind of urban areas. This is reflected in the explicit inclusion of kinetic models of the oxidation of the various hydrocarbons listed above. While their treatment of C_3H_6, C_2H_4, C_2H_2, C_4H_{10}, nC_6H_{14}, and CH_4 follows well known lines (see, e.g., Demerjian et al., 1974, and Hendry et al., 1978), the formulation of m-xylene oxidation differs significantly from other descriptions of the kinetics of aromatic compounds (Hendry, 1978). The net thrust of Hov and Isaksen's approach seems to cause m-xylene to induce a higher rate of NO oxidation. In effect, m-xylene is made to appear to be more reactive than is thought to be the case, which implies that ozone production attributed to m-xylene would be overestimated. However, the reports of applications of Hov and Isaksen's model do not discuss the contribution of individual hydrocarbons to ozone formation; hence, we cannot establish the importance of m-xylene in the overall mechanism. All that can be said at this time is that there may be a potential problem associated with m-xylene, which could alter any inferences drawn from applications of this model.

The model developed by Graedel and Allara is similar to the others, in that it is a chemical model that allows the mixing volume to change. The species are assumed to be instantaneously and uniformly mixed within the volume; in essence, it is a box-type model. The chemical module is highly detailed, containing over 300 reactions involving more than 200 chemical species. A unique feature of this model is the inclusion of reaction sets for alpha-pinene and isoprene. It also includes CH_4, hydrogen sulfide, ammonia, and aldehydes. Thus, the model is intended for studying the contribution of local photochemistry and sources on nonurban ozone levels. It can also be used to examine the impact on ozone of urban NO_x.

2. Model Verification

None of the models has undergone adequate verification tests against field data; this is partly due to the sparseness of the data available. Chang and Weinstock's model has been tested against smog chamber data in a limited fashion. We found no evidence of verification attempts by Chameides, Liu, or Fishman and Crutzen. Hov et al. (1978) compared the predictions of Hov and Isaksen's model against O_3 and NO_2 data collected in England and Ireland on 29 and 30 August 1974. The comparison is encouraging because calculations and observations are within a factor of two. However, the test is inadequate because it employs only four observations, which is too small a sample to yield meaningful conclusions. The same applies to other comparisons reported by Isaksen et al. (1978 a,b). In one test, Hov and Isaksen's model predicted ozone concentrations in the St. Louis urban plume with a maximum error of about 30 percent, with most of the differences between computation and observation being considerably smaller (Isaksen et al., 1978b).

Graedel and Allara (1976) report limited tests of their model against field data that yielded agreement to within a factor of about three for most species, the conspicuous exception being ozone, which was underpredicted by a greater margin. They attribute the ozone discrepancy to the fact that nonurban ozone is not produced solely by local photochemistry, but is also transported, ready-made, from other areas. The transported ozone would be expected to combine additively with the locally made ozone. Since the model considers local effects only, it seems reasonable that ozone would be underestimated.

The quantitative reliability of the models remains an open question. Because of this, the models must be considered speculative but nonetheless potentially useful tools for studying NO_x/O_3 interactions in nonurban areas. Predictions obtained using these models can best be interpreted as qualitative indications of potential effects.

H. Relationship Between NO_x and O_3

Several hypotheses have been proposed to explain the rural ozone phenomenon. Reduced to essentials, the hypotheses are:

- O_3 is locally produced from existing and transported precursors.
- Ozone is formed in urban plumes and transported to nonurban areas.
- Rural ozone results from natural causes, such as stratospheric intrusion.

It should be recognized, however, that rural ozone is due to a combination of factors, rather than to a single mechanism. Consequently, the hypotheses are complementary rather than mutually exclusive. Thus, the problem becomes one of attempting to find a predominant mechanism among a variety of causes. For our purposes, we examine below various aspects of the first two postulates.

Before proceeding to review the literature, we note that (for regulatory purposes) a basic question about the role of NO_x in ozone formation in nonurban areas is whether such ozone production is NO_x-limited. Ozone formation is said to be NO_x-limited when addition of NO_x results in higher ozone concentrations. However, the NO_x-limited condition is a function not only of NO_x, but also of the hydrocarbon concentration. The situation is illustrated in Figure 2, which plots O_3 as a function of NO_x with nonmethane hydrocarbon (NMHC) as a parameter. The figure shows that O_3 increases with NO_x until it reaches a maximum, decreasing thereafter with further increases in NO_x. Whether ozone increases or decreases with increasing NO_x is determined by the NMHC/NO_x ratio. The figure shows that for NMHC/NO_x ratios greater than about 4.8, ozone will be in the NO_x-limited condition, and vice versa. The precise NMHC/NO_x ratio that forms the boundary of the NO_x-limited region will vary depending on the type of hydrocarbons involved (the curves in Figure 2 are for a mixture of propylene and n-butane), so no special significance attaches to the ratio of 4.8. Nevertheless, atmospheric values of

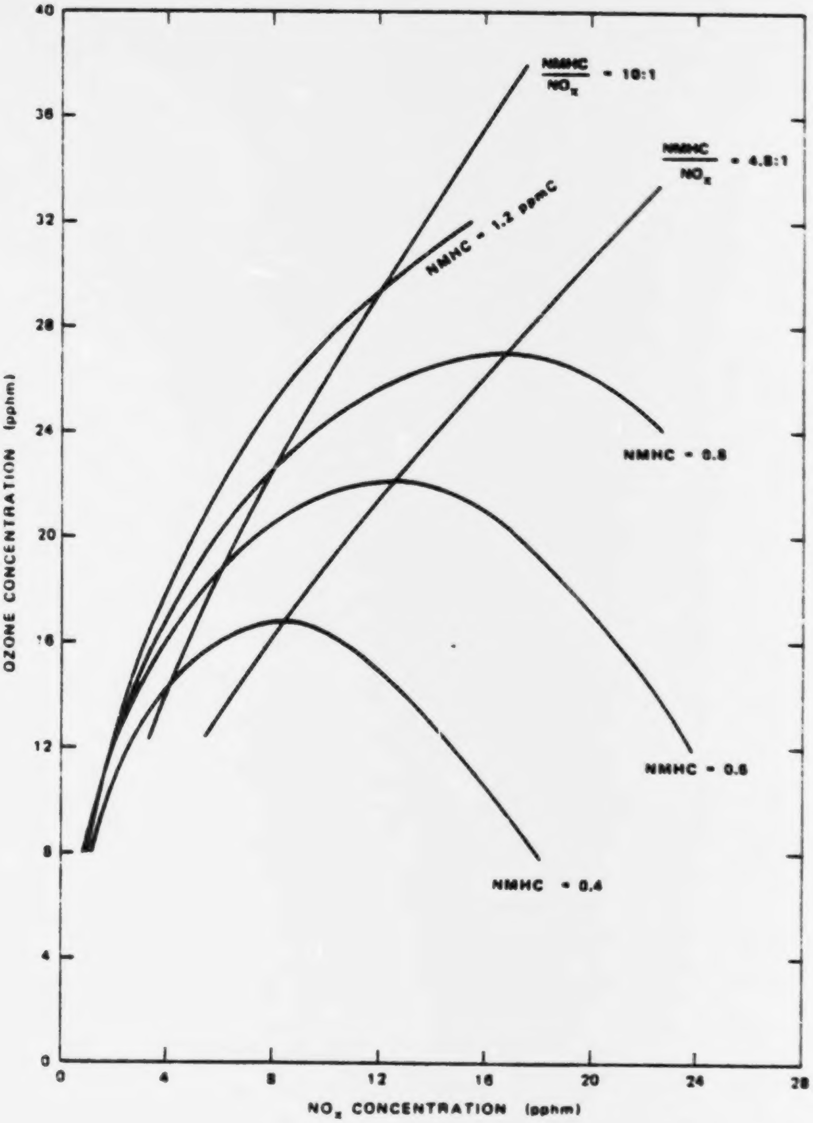


FIGURE 2 OZONE CONCENTRATION AS A FUNCTION OF NO$_x$ LEVEL WITH NONMETHANE HYDROCARBON (NMHC) AS PARAMETER

$NMHC/NO_x > 10$ generally lead to NO_x-limited conditions for O_3 formation. Thus, a high $NMHC/NO_x$ ratio is a necessary condition for ozone to be in the NO_x-limited region.

If O_3 formation in nonurban areas is NO_x-limited, then the possibility exists that increases in NO_x emissions from urban areas may enhance ozone levels in nonurban regions downwind of the NO_x source. Hence, to reduce nonurban ozone, it would be necessary to control urban NO_x emissions. On the other hand, the case for controlling NO_x emissions is less compelling if nonurban ozone levels are not NO_x-limited. This is the fundamental problem that motivates the literature review described below.

The literature contains conflicting reports on whether adding NO_x enhances, inhibits, or has no effect on ozone formation. The most direct evidence of enhancement due to addition of NO_x has been recently reported by Miller et al. (1978), who used an airplane to track a power plant plume over Lake Michigan for four hours--a distance of about 90 miles. As expected, ozone in the NO_x-rich plume initially was below ambient levels, the latter being about 90 ppb and the former approximately 60 ppb. After about one hour, ozone in the plume began to surpass ambient levels, and continued to accumulate. After four hours, ozone levels in the plume reached about 150 ppb compared to 100 ppb for the ambient. The authors offer plausible evidence that the apparent cause of this phenomenon was the addition of NO_x to an atmosphere with a $NMHC/NO_x$ ratio that was very high $\approx 30/1$) initially. With such high $NMHC/NO_x$ ratios, ozone production is NO_x-limited. Hence, as the NO_x from the plume mixes with the surrounding air, the extra NO_x enhances ozone formation. It seems reasonable to expect that the type of hydrocarbons present would determine the threshold that the $NMHC/NO_x$ ratio has to exceed for the system to be in the NO_x-limited region of ozone formation. Unfortunately, no hydrocarbon composition data are given in the published report. Lacking such data, it is risky to attempt to formulate any general rules. Nevertheless, the fact remains that ozone enhancement did occur, and that it appears to be directly related to the addition of NO_x. Thus, under the proper conditions, similar phenomena can occur in nonurban areas impacted by urban NO_x.

Jeffries et al. (1976) provide indirect evidence in support of the concept of NO_x-enhanced ozone production in nonurban areas. Their investigation used an outdoor smog chamber irradiated by sunlight. Some of the experiments involved extended irradiations over several days in succession. Their experiments indicate that first-day ozone production is dominated by the initial hydrocarbon concentration. However, second-day ozone levels can be as high as the first day's, even though most of the alkenes were consumed the first day. The implication is that an aged air mass essentially devoid of alkenes can retain the capacity to produce substantial amounts of ozone given a small amount of NO_x. They estimate that the amount of NO_x required to produce such behavior is of the order of 5 ppb. However, we have seen in Table 3 that 5 ppb is typically observed in rural areas. Hence, if their conclusions are correct, the chemical conditions may already exist that favor local ozone generation in nonurban areas.

To investigate the effects of dilution, Jeffries et al. (1976) performed a three-day experiment in which the initial charge of the chamber was irradiated and diluted with purified air until only 5 percent of the original mass remained. The remainder was irradiated by sunlight for two successive days, and produced significant amounts of ozone, but generally less than in the first day. These results lend credence to the hypothesis that ozone production can occur in an air mass that has been transported over a long distance, in spite of the substantial dilution that the pollutants undergo.

An independent study by Ripperton et al. (1976), also using an outdoor smog chamber, supports the conclusions of Jeffries et al. (1976) mentioned above. Ripperton et al. concluded that NO_x levels in the 1- to 5-ppb range can generate substantial amounts of ozone. Their results also parallel Jeffries with regard to dilution effects.

Although highly suggestive, these results should be interpreted with great caution owing to the uncertainties associated with wall effects in smog chambers. Thus, it is generally recognized that the walls can act as a source of free radicals that act to initiate the hydrocarbon oxidation chain, thereby inducing a level of photochemical activity that may not be representative of atmospheric conditions.

While the previous studies suggest that low levels of NO_x can sustain, and that additional NO_x may enhance, local ozone production in rural areas, a report by Lonneman (1976) concludes that ozone transport from urban areas may be the dominant factor in determining rural ozone levels. Lonneman discusses ozone, NO_x, and hydrocarbon measurements in Wilmington, Ohio, a rural site surrounded by three metropolitan areas. The key evidence indicating that transport predominates is that the high ozone values occurred in the late afternoon and early evening. This certainly suggests that a polluted air mass arrived at the site, since local ozone generation is tightly coupled to the sunlight cycle. Thus, a locally generated ozone maximum would occur around noon, at the time of the peak in solar radiation intensity, rather than in the late afternoon or early evening. It would have been interesting to see whether the days containing the late ozone peak also displayed an earlier peak around noon, but this is not discussed by Lonneman. In Section IV of this report we examine some recent field data that show this double-peak phenomenon.

That ozone is transported over hundreds of kilometers is by now a well-documented phenomenon. The literature on this subject is extensive and growing; some references of interest are Blumenthal et al. (1974), Cox et al. (1975b), Decker et al. (1977), White et al. (1976), Westberg et al. (1978 a,b,c), Spicer et al. (1976a), Research Triangle Institute (1976), and Kauper and Niemann (1976). The reader should consult the references for descriptions of the transport mechanism; here we summarize the effects associated with transported ozone. In general, it appears that transported ozone combines additively, rather than synergistically, with local ozone to increase the overall concentration at the ground. This higher level can exceed the ambient standard; in some cases, the transported ozone by itself exceeds the standard. Ozone transport can occur over several days, but the evidence suggests that single-day transport may be a predominant influence because of losses that occur as ozone is subjected to chemical scavenging and dry deposition processes near the ground. Hence regeneration of ozone seems to be required on a daily basis to sustain transport of high ozone concentrations over several days. Thus, while transported ozone can be responsible for high downwind ozone levels observed within a travel time of 24 to 36 hours, the availability of ozone precursors may be necessary to extend the transport range. These precursors may well be carried along with the ozone itself, since the evidence suggests that an "aged" or "spent" polluted air mass can continue to form ozone. Alternatively, the precursors may be present already at the downwind location, for (as we have seen) NO_x levels of 1 to 10 ppb prevail in rural areas and such levels are sufficient to form significant quantities of ozone, provided that the necessary hydrocarbons are also available. Thus, in examining the role of NO_x in nonurban ozone formation, the concentrations and types of hydrocarbons that are present at the rural sites must also be considered. A full review of this aspect of the problem is beyond the scope of this report, and we shall only take a brief look at it.

Both natural and anthropogenic hydrocarbons are found in rural areas of the United States. The role of natural hydrocarbons (NHC) in the formation of nonurban ozone is a subject of considerable controversy (cf. Coffey and Westberg, 1977; Lonneman et al., 1978 and 1979; Sculley, 1979; Ludlum and Bailey, 1979). Some researchers believe that NHC are unimportant, while others assert that further research is needed to prove or disprove this hypothesis. Others have used statistical arguments to postulate that NHC are significant contributors to urban and suburban smog, a contention that has been hotly debated (Sandberg et al., 1978 and 1979a,b; Bufalini, 1979; Miller et al., 1979). A recent study by Arnts and Gay (1979) examined the photochemistry of selected NHC, including isoprene, p-cymene, and six monoterpenes. The investigation was aimed at estimating the ozone-forming potential of these NHC in the presence of NO_x in a controlled laboratory environment. They conclude that monoterpenes do not permit ozone to accumulate because of the fast reaction between ozone and monoterpenes, which agrees with suggestions previously advanced by Westberg (Coffey and Westberg, 1977). Isoprene was found to produce significant amounts of ozone, but not at high carbon/NO_x ratios, where some ozone suppression was observed. However, the hydrocarbon concentrations used in the experiments were higher than have been observed in the atmosphere, and the results of the study, while suggestive, can not be readily extrapolated to the atmospheric milieu. In view of the wide difference of opinion, it is clear that nothing definitive about the role of NHC can be said at this time, which leaves the anthropogenic component to be dealt with.

Light alkanes (e.g., butanes, pentanes, and ethane) and alkenes (e.g., ethylene) have been observed in rural areas. Spicer et al. (1976a) report 3-hour average NMHC levels at a rural site downwind of Dayton, Ohio, ranging from 0.67 to 0.72 ppmC. Ethane, ethylene, and acetylene were also detected at the same site, the latter being an indicator of anthropogenic influence since it is primarily emitted by automobiles. Decker et al. (1977) measured hydrocarbons aloft in the St. Louis urban plume that was tracked with a balloon. While their data contain some anomalies (e.g., one sample was reported to contain 1016 ppbC propane and 112.6 ppm of CH_4), they do provide an indication of the hydrocarbon levels that are present in a plume under transport conditions. Table 8 shows the concentration range of several compounds during the day and night portions of the balloon's flight. It is evident that the alkenes and propylene were present in small but significant quantities during the overnight portion of the flight. During this period, ozone remained essentially constant at about 125 ppb; hence, there appears to have been very little ozone lost through O_3-alkene reactions. The general meteorological conditions consisted of a subsidence inversion aloft and a strong radiative ground-based inversion, conditions that favor long-range transport. Thus, not only is ozone transported, but the hydrocarbons are also carried along, and will be available to participate in the photochemical smog process the next day,

Table 8

RANGE OF HYDROCARBON CONCENTRATIONS MEASURED ABOARD DA VINCI II BALLOON*

Compound	Concentration Range (ppbC)		
	Daytime 8 Jun 1976 1100 - 1900	Nighttime 8-9 Jun 1976 2000 - 0600	Daytime 9 Jun 1976 0600 - 0800
Propane	2.9 - 3.9	2.5 - 10.5	3.8 - 40.0
Isobutane	1.0 - 3.1	1.1 - 8.8	3.7 - 5.1
n-Butane	6.4 - 11.8	5.0 - 20.6	10.6 - 65.2
Isopentane	1.8 - 39.8	0† - 12.2	5.4 - 8.3
Acetylene	0.9 - 6.1	2.2 - 4.8	3.3 - 5.4
Propylene	1.5 - 8.8	0.8 - 3.4	1.5 - 13.7
1-Butene	0† - 3.2	0† - 5.4	0.5 - 34.6
Trans-2-Butene	0† - 2.0	0† - 2.0	0† - 8.4

*Adapted from Decker et al. (1977). Four out of 22 samples have been excluded due to anomalous concentrations.

†Zero concentration denotes levels below limit of detection.

when all the species undergo fumigation upon the breakup of the inversion.

Additional evidence of the presence of hydrocarbon precursors at a rural site is given in Table 9, which lists average concentrations of several compounds measured in Elkton, Missouri (Rasmussen et al., 1977). It is apparent that acetylene, propylene, and 1-Butene are at the lower end of the concentration range observed in the St. Louis plume (cf. Table 8). The same is true for the butanes and isopentane. However, propane levels are comparable to the St. Louis data. Obviously, Elkton

Table 9

AVERAGE HYDROCARBON CONCENTRATIONS
IN ELKTON, MISSOURI

Compound	Concentration (ppbC)
Propane	5
Isobutane	2
n-Butane	3
Isopentane	3
n-Pentane	2
Ethane	5
Acetylene	1
Propylene	1
1-Butene	0
Ethylene	2

*Adapted from Rasmussen et al. (1977).

is cleaner than an urban plume, but it still shows evidence of anthropogenic influence. This suggests that some hydrocarbon precursors of ozone are as ubiquitous as NO_x.

Two very useful studies by Ludwig et al. (1976; 1977) and one by Meyer et al. (1976) investigated the relationship between rural ozone and transported precursors. Ludwig examined high ozone concentrations at several rural sites by analyzing the emission and meteorological history of the air masses arriving at the sites. In general, it was found that NO_x emissions were positively correlated with ozone. The overall correlation was low (0.27 and 0.32 for two different time lags) but highly statistically significant, and one site showed a correlation of 0.64. By contrast, hydrocarbon emissions showed no significant correlation with ozone. The analysis showed that NO_x emitted within 12 hours and between 24 and 36 hours prior to the arrival of the air mass at the site had the most influence on ozone. These time lags respectively reflect the impact of nearby emissions (0 to 12 hours) and long range transport (24 to 36 hours). A half-life of NO_x of at least one day is suggested by these time intervals, which is consistent with the range of estimates previously mentioned in Section II-D. From Ludwig's work, we can infer that ozone levels at rural sites are probably enhanced by addition of NO_x, which implies that ozone production is NO_x-limited. This further suggests that high NMHC/NO_x ratios exist at these rural sites, and that the prevailing concentrations of NMHC are sufficient to promote the formation of substantial amounts of ozone. While these inferences cannot be considered definitive, they are consistent with the findings of other studies.

Meyer et al. (1976) independently studied ozone levels at urban and rural sites using a trajectory approach similar to Ludwig's. Their results parallel Ludwig's, showing that NO_x emissions with a 6-hour time lag are positively correlated with ozone at rural sites. The overall correlation is low (0.23), but statistically significant. Moreover, it is noteworthy that lagged NO_x emissions were not significantly correlated with ozone at the urban sites, whereas the unlagged emissions were correlated. This latter result is precisely what would be expected in view of the disparate distance scales that prevail between sources and receptors in urban and rural areas. Meyer's analysis also showed that hydrocarbon emissions with lags of 24 and 30 hours showed a positive correlation with ozone at the rural sites of the same magnitude as for NO_x. This is rather puzzling, as one would expect to see hydrocarbon-ozone correlations with short time lags as well; it also contradicts Ludwig's results. Thus, these results indicate that at the rural sites NO_x emissions from sources that are relatively close to the site are more important than from sources that are far away, while the opposite is indicated for hydrocarbons. This may be a consequence of the geography of the sites analyzed, and further investigation is required to confirm this effect. For NO_x, the positivity of the correlation indicates that ozone levels will tend to be enhanced by the addition of NO_x, which is the same qualitative effect indicated by Ludwig's analysis. Thus, Meyer's study supports the hypothesis that ozone formation in rural areas may well be NO_x-limited.

Various attempts have been made to model rural ozone formation. Chameides (1978) used his model to examine the effect of the rate constant of the reaction $HO_2 + NO \rightarrow NO_2 + HO$, which has been recently revised upward (Howard and Evenson, 1977). He concluded that with the higher rate constant (approximately 1.2×10^4/ppm/min levels of NO_x below 1 ppb are sufficient to promote the formation of substantial amounts of ozone. However, his work was limited to steady-state estimates using CH_4 as the sole source of organic radicals; hence we must discount the quantitative aspects of this work and consider only the qualitative effects. Nevertheless, it is generally agreed that the faster reaction $HO_2 + NO \rightarrow NO_2 + HO$ enhances the ability of NO_x to generate ozone since in all photochemical smog mechanisms this reaction is one of the key steps (another being $RO_2 + NO \rightarrow RO + NO_2$) that oxidize NO to NO_2.

Graedel and Allara (1976) report that increasing NO_x emissions would result in a small decrease in peak ozone. This is contrary to the hypothesis that ozone production in rural areas may be NO_x-limited. However, their model used the lower $HO_2 + NO$ rate constant; hence, their result may be subject to revision. Liu (1977) also reported a decrease in ozone due to increased NO emissions, but he also used the outdated rate constant for $HO_2 + NO$.

Recently, Cleveland and Graedel (1979) have examined the impact of changing NO emissions on ozone downwind of urban areas in the northeast United States. They conclude that increasing NO will initially depress urban ozone levels, but is likely to enhance ozone concentrations downwind. Conversely, reductions in urban NO emissions will increase ozone within the source region, but will probably lead to lower ozone levels downwind. Their results also indicate that, in the northeast, controlling NO emissions is more effective than hydrocarbon controls as an abatement strategy for photochemical pollutants. These results address directly the problem that concerns us, and imply that NO_x emissions should not be allowed to increase in the northeast because nonurban ozone pollution will become worse. However, the conclusions of Cleveland and Graedel are based on extrapolations of model predictions and require further work to test their validity. Nevertheless, their results agree qualitatively with studies previously discussed, notably Ludwig et al. (1976, 1977) and Meyer et al. (1976), which also suggest a positive relationship between NO_x emissions and nonurban ozone.

Isaksen et al. (1978a) examined the problem of ozone production in an urban plume using NMHC/NO_x ratios of 4 and 0.01 with a constant total emission strength. These ratios are at the lower end of the range of ratios usually found in urban areas, which range from 2 to 50 with a median ratio of 10. (In fact, ratios of 4 and 0.01 are seldom observed in urban areas.) As expected, the higher ratio yielded more efficient ozone production per molecule of NO_x, and resulted in higher ozone concentrations downwind. This implies that increased NO_x emissions would lower ozone downwind, provided that hydrocarbon emissions are not augmented in the same ratio. From these results one might conclude that nonurban ozone production is not NO_x-limited, but NMHC-limited instead. While this may be true in the short term, the conditions can change drastically in the long term. Thus, with high NO_x emissions and a low initial NMHC/NO_x ratio, the hydrocarbon consumption is very slow (this is, of course, the cause of the low ozone). This results in a substantial residue of unreacted hydrocarbons, accompanied by a gradual but steady increase in the NMHC/NO_x ratio. The net result is that the plume can retain its ozone production potential for several hours, and the eventual high NMHC/NO_x ratio turns the situation around: from NMHC-limited to NO_x-limited conditions. The situation is thus analogous to that described by Miller et al. (1978) in the power plant plume over Lake Michigan. Thus, contrary to Isaksen's results, the possibility remains that adding NO_x can enhance ozone production downwind, which is consistent with the results of Cleveland and Graedel (1979) previously discussed.

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III SUMMARY OF EXPERT OPINION

A. Introduction

In assessing the state of knowledge about nonurban NO_x/O_3 interactions, SRI contacted leading researchers to obtain information about recent developments in the field. Such a survey of expert opinion helps not only to update the published record, but also identifies areas of uncertainty where further research is required. The latter point is helpful in establishing research priorities.

In this survey, a number of investigators representing government, private, and academic institutions were contacted. Of those who indicated interest in participating, eight subsequently submitted replies to our questions; their names are listed elsewhere in this document. However, no individuals are quoted in the text. The responsibility for the interpretation of the replies is ours.

The survey questionnaire contained 35 questions covering five general categories: measurement methods, sources and sinks of NO_x, chemical aspects, control strategies, and identification of knowledge and data gaps. Not all respondents answered all the questions. In what follows, we summarize the replies received, and provide some additional comments and explanatory remarks.

B. Summary of Results

1. Measurement Methods

In this category, the participants were asked to evaluate the quality of routinely collected NO_x data for various concentration ranges. The replies are shown below:

Range of NO_x Levels (ppb)	Assessment of Data Quality
<1	Poor
1-5	Fair to poor
6-10	Good to fair
>10	Excellent to good.

This evaluation makes it apparent that the NO_x data in the higher concentration ranges is generally reliable. While this is encouraging for urban data, it warns that rural and remote measurements below 6 ppb should be treated with caution.

Respondents offered the following comments about NO_x data:

- Use of wet chemical methods should be discontinued for routine monitoring.
- NO data are generally better than NO_2, but can be poor below 10 ppb because of difficulties with zero-setting techniques.
- NO_2 data are subject to interference from other gases. This problem is especially important for late afternoon measurements.

As a postscript, we note that wet chemical (i.e., colorimetric) instruments are being gradually replaced by chemiluminescent detectors for routine monitoring applications. Recent work at SRI compared simultaneous chemiluminescent and colorimetric NO_2 measurements made at three urban sites in California during 1975-1977 (Martinez and Nitz, 1979); the comparison was performed for NO_2 levels that exceeded 200 ppb. Colorimetric and chemiluminescent measurements were found to be linearly correlated at two of the three sites, the correlation coefficients being 0.71 and 0.86. At these two sites it was also found that the chemiluminescent data tended to be greater than the corresponding colorimetric concentrations. The third site showed no correlation between the two instruments. For the concentration range considered, these results show that NO_2 data obtained using colorimetric and chemiluminescent techniques may not be strictly comparable; additional work is required to test this conclusion for NO_2 levels below 200 ppb.

2. Sources and Sinks of NO_x

The questions in this category were aimed at:

- Obtaining estimates of the half-life of NO_x
- Identifying NO_x removal mechanisms
- Evaluating the importance of indirect sources of NO_x;
- Obtaining a qualitative assessment of the relationship between NO_x sources and atmospheric concentrations.

The questions and replies are first given below, and our comments follow.

- Estimates of half-life of NO_x
  - Six to twenty-four hours in the boundary layer.
  - One to two days in the free troposphere.
- Important removal mechanisms
  - Heterogeneous removal through dry and wet deposition may be the most important mechanism.
  - Gas phase reactions $HO + NO_2 \rightarrow HNO_3$ and $RCO_3 + NO_2 \leftrightarrow PAN$.
- Indirect Sources of NO_x
  - Anthropogenic NH_3 emissions are considered to be trivial as an indirect source of NO_x through conversion of NH_3 to NO_x.
  - All indirect sources (including NH_3), are generally unimportant factors in contributing to the total tropospheric NO_x burden.
- Assessment of PAN as a reservoir for NO_x. It is likely that PAN can act as a reservoir for NO_x.
- Assessment of the relationship between NO_x emissions and atmospheric levels:
  - In suburban atmospheres, NO_x emissions and ambient levels are directly related. However, atmospheric levels tend to be lower than expected from estimated emission rates. Local (suburban) sources can predominate.

- In rural atmospheres, NO_x levels are weakly influenced by urban sources. Local sources are most important determinants of ambient concentrations of NO_x.
- In remote atmospheres, NO_x concentrations are generally unaffected by man-made sources, because of the short half-life of NO_x. Infrequent high concentrations are due to transport from anthropogenic sources.*

Regarding the half-life of NO_x, the range of estimates given above is at the lower end of the 1- to 20-day estimate mentioned in Section II-D. This is consistent with suggestions that residence time estimates should be revised downward in light of the discovery that background levels are below 1 ppb (rather than several ppb) as previously believed (cf. Section II-C and Ritter et al., 1978).

Residence time estimates are related to the removal mechanisms. Thus, it is instructive to note that the half-life of NO_x due to gas phase losses only (primarily OH attack) is estimated to be between seven and fifteen hours. For dry deposition, velocities of about 0.3 cm/s have been suggested. Under the appropriate circumstances, (viz., a shallow mixing layer and moderate mixing within the layer), such a velocity can result in a half-life as low as three hours, thereby overwhelming gas phase losses. For comparison, the ozone half-life has been estimated to be about 30 hours (Ripperton et al., 1976). However, near the ground, ozone deposition velocities as high as 1 cm/s have been estimated, (Harrison et al., 1978), which can lead to a half-life as short as one hour. Thus, when the aggregate effect of all removal processes is considered, it is probable the half-life of NO_x within the mixed layer is comparable to that of ozone.

In Section II-F we discussed the potential impact of indirect sources as contributors to the overall NO_x burden. In that discussion, conversion of ammonia to NO_x was estimated to constitute about 10 percent of the total burden. The reply to our questionnaire could be interpreted as being at variance with the literature, because 10 percent is not necessarily a trivial contribution. However, as noted in Section II-F, the $NH_3 \rightarrow NO_x$ conversion process is poorly understood, and its occurrence has been questioned. The replies to the questionnaire apparently reflect the latter view.

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*While it may seem contradictory to state that "remote" areas are impacted by anthropogenic sources, such a statement merely reflects the fact that few, if any, areas in the United States are totally free from air pollution.

The reversible reaction $RCO_3 + NO_2 \leftrightarrow$ PAN suggests the possibility that PAN can act as a reservoir for NO_2 by (in effect) "storing" NO_2, only to return it later upon decomposing. The reply to the question indicates that this process is now considered to be likely to occur. If this is correct, the transport range of NO_x would be affected since PAN may be longer-lived than NO_2 under the proper conditions. However, the atmospheric half-life of PAN depends strongly on temperature and on the NO_2/NO ratio. Table 10 shows estimates of the half-life of PAN obtained by Hendry and Kenley (1978). Based on these data, it is conceivable

Table 10

ATMOSPHERIC HALF-LIFE OF PAN*
(Hours)

Temperature (°C)	NO_2/NO Ratio			
	0.1	1.0	10	100
12	4.5	5.5	17	140
22	0.9	1.1	3.5	28
32	0.2	0.24	0.8	6.2

*Adapted from Hendry and Kenley (1978).

that in an urban plume undergoing transport at night, the NO_2/NO ratio and the temperature may be such that PAN can have a half-life of several hours, and thus could travel a reasonably long distance. The next day, PAN would decompose rapidly as the temperature increased, thereby acting as a source of NO_2 and RCO_3. The latter could participate in the oxidation of NO (given a low NO_2/NO ratio), which would eventually result in enhanced ozone levels. Thus, PAN may be a pool not only of NO_2, but also of RCO_3, and both of these compounds help to promote O_3 formation. While the participants in the survey believe that this process is likely to occur, many uncertainties remain and further investigation is needed. In particular, we need to estimate the concentration of PAN that might survive after transport and dilution. Finally, it should be noted that other organic peroxynitrates may undergo similar processes. One respondent commented that organic peroxynitrates are potential reservoirs of odd nitrogen, and that their formation and stability should be studied further.

The replies to the question about the relationship between emissions and ambient levels of NO_x seem to reflect the view that transport of NO_x from urban areas is important only in suburban locations. This view is compatible with the belief that the half-life of NO_x is too short to allow any significant transport to occur. On the surface, it appears that this view rules out the hypothesis that local ozone synthesis in rural areas is influenced by precursors transported from urban regions. This is not necessarily the case, however, because (as we have seen) the evidence suggests that low levels of NO_x are sufficient to produce substantial amounts of O_3 in rural areas (assuming the necessary NMHC is available). Thus, even though dispersion may obscure or weaken the link with urban emissions, the small amounts of urban-generated NO_x that reach the countryside could still play a significant role in local ozone production. This argument is not meant to imply that local rural sources of NO_x are not important -- they are -- but rather that the residue from urban emissions cannot be dismissed as a contributing factor in local ozone synthesis.

3. Chemical Aspects

The questions posed in this category were intended to elicit judgments about a few specific topics, rather than to range over a broad panorama of chemical kinetics. The questions and answers are given below and are followed by our comments.

- Photochemical Models for Nonurban Areas
  - Reliability and verification: Photochemical models for nonurban environments were judged to be essentially unreliable. Respondents also view the models as being basically unverified.
  - Critical Chemical Parameters: The following reactions were suggested as being critical in the sense that model performance would be significantly affected if their rate constants were modified:
    - * Surface reactions
    - * $RO_2 + O_3$
    - * $RO_2 + NO$
    - * $HO_2 + NO$
    - * $HO_2 + NO_2$
    - * $HO + NO_2$.
- Use of smog chambers for determining NO_x/O_3 interactions in nonurban areas: Smog chambers were judged to be fairly adequate for establishing the involvement of NO_x in O_3 formation in nonurban areas.
- Relationship between NO_x and nitrates: NO_x and nitrates are related, but the relationship is probably nonlinear. However, there is no relationship between coexisting concentrations. HNO_3 and some organic nitrates may serve as pools for NO_x, which can be transported long distances; this would likely yield low NO and NO_2 levels in remote areas.
- NO_x reactions important in nonurban atmospheres: The following reactions or processes were judged to be more important in a nonurban environment than in the urban atmosphere:
  - $HO_2 + NO \rightarrow HO + NO_2$
  - Formation of HNO_3.
- Role of natural hydrocarbons in rural O_3 formation: This question yielded several answers, demonstrating a split opinion on this topic. The answers are shown below. (The order in which the replies are listed has no particular significance.)

  - Natural hydrocarbons are probably very important, but emission data are needed for a complete assessment.
  - If present, natural hydrocarbons should contribute to O_3 formation.
  - Some natural hydrocarbons, e.g., terpenes, consume O_3, and the net effect may be that O_3 is destroyed.
  - Natural hydrocarbon levels in ambient air are too low to play a significant role in ozone formation.

- Effect of ozone intrusion on photochemistry in nonurban atmospheres: The question asked for a judgment about the likelihood that ozone intrusion from an external source (e.g., the stratosphere) might accelerate the photochemistry in nonurban atmospheres. Two contradictory judgments emerged, some respondents replying that it would be unlikely, and some that it would be likely.

We included the questions about photochemical models partly because several hypotheses advanced about nonurban ozone rest on results obtained from models, and partly because some of the participating scientists have developed and applied models and their judgment would be especially valuable in assessing the reliability of the various models. The response to the questions of reliability and verification agrees with our earlier remarks in Section II-G. The implication is that continued research on model development and verification is necessary in order to improve reliability. This is imperative because models can be extremely useful in unraveling the complex interactions.

While photochemical models in their present state of development were judged to be essentially unreliable for application to nonurban areas, smog chambers were considered to be fairly adequate for a similar use. These two responses appear to be inconsistent, since the chemical component of the models is normally tested using smog chamber data. We believe that there is no inconsistency, in that the judgment about the models is probably based on the perception that the verification tests of the models have not gone far enough.

Somewhat akin to the application of models is the use of smog chambers to elucidate chemical effects: Both have their problems, but must be used because of the complexity of the problem. The qualified judgment of adequacy bestowed on smog chambers for application to a nonurban environment is encouraging, both for model development and for the assessment of chemical effects based on smog chamber data.

Regarding the relationship between NO_x and nitrates, the replies reiterate a theme mentioned earlier about the potential of some nitrates to serve as reservoirs for NO_x. Given that the same suggestion was made independently by several individuals, it appears that this possibility merits further investigation. In the context of nitrates and other products of NO_x, the reader should consult the work reported by Spicer (1976; 1977) and Spicer et al. (1976b; 1977).

The divergent replies to the question about the role played by natural hydrocarbons in rural ozone production reflect the current debate that surrounds this topic, a glimpse of which was seen in Section II-H. It is apparent that the last word on this subject has not been written.

The question about the effect of ozone intrusion was prompted by suggestions in the literature (e.g., Hathorn and Walker, 1976) that such additions of ozone may help trigger ozone episodes by speeding up the photooxidation processes, hence the term "acceleration." If it happens at all, such a phenomenon would be more likely in an urban setting where unreacted alkenes exist. Assuming that the concentration of the injected ozone is high enough, the O_3 + alkene reactions would yield peroxy radicals that in turn oxidize NO, a process that could eventually result in a fast ozone buildup. However, such favorable conditions are unlikely to exist in nonurban areas, where alkene levels tend to be low. On this basis, it seems reasonable to conclude that O_3 intrusions in nonurban locations would simply add to the total ozone load, instead of promoting additional local synthesis.

4. Control Strategies

This category contained questions intended to obtain judgments about the effectiveness of using NO_x controls as an ingredient of an oxidant control strategy. In addition, we inquired about the appropriateness of applying a popular methodology, the so-called isopleth method, in a nonurban setting. Questions, replies, and comments follow.

- Estimate the likelihood that control of NO_x emissions will substantially reduce photochemical air pollution in urban and nonurban locations: Although the replies were diverse, the consensus was that NO_x controls would be generally ineffective in controlling ozone in urban regions, but could be moderately effective in nonurban areas.
- Can the isopleth method for estimating O_3 from NO_x and NMHC precursors be extended for use in nonurban settings? The response was negative.

Regarding the first question, one participant also commented that introduction of NO_x into rural areas might well trigger O_3 problems where there are none, and could aggravate existing problems. Thus, the view seems to be that anthropogenic NO_x emissions are at least partly responsible for the elevated ozone levels that are observed in nonurban areas. This is consistent with some of the findings of Section II-H. (cf. Ludwig et al., 1976; 1977; Meyer et al., 1976; Cleveland and Graedel, 1979).

5. Identification of Areas Requiring Further Research

The participants were asked to name subjects where, in their view, important knowledge or data gaps exist with regard to the relationship between NO_x and O_3 in suburban, rural, or remote locations. They are shown below grouped in an approximate order of importance. It should be noted that the topics within a particular group should be considered equally important, i.e., it is the order of the four groups that is of some consequence, not that of individual topics.

IMPORTANT KNOWLEDGE OR DATA GAPS

NO_x sinks
Natural sources of NO_x
Role of natural hydrocarbons

NO_x measurements
NO_x residence time in the atmosphere
Natural sources of O_3

Atmospheric residence time of O_3
Basic NO_x chemistry

Rate constants
O_3 sinks

The order of the groups reflects rather faithfully those areas which were described earlier as being generally uncertain (cf. Section II). Thus, the first group includes natural hydrocarbons, whose rather controversial status has already been mentioned. As regards priorities, we would go further and aggregate the first six topics into one group, and the last four into another. However, it should be recognized that the differences in priorities are slight -- all the topics need further research. It must also be realized that the suggested priorities do not necessarily coincide with regulatory objectives. Thus, the list of topics requires additional screening from a regulatory standpoint.

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IV ANALYSIS OF DATA
FROM THE SULFATE REGIONAL EXPERIMENT (SURE)

A. Introduction

The SURE is an extensive air quality monitoring and analysis program sponsored by the Electric Power Research Institute (EPRI) designed to establish the relative importance of emissions from various source categories in contributing to regional ambient sulfur dioxide (SO_2), particulate sulfate, and NO_x (Mueller et al., 1977). To this end, a regional network of monitoring stations was established to obtain a data base of pollutant concentrations. The overall program is being conducted for EPRI by the firm of Environmental Research and Technology Inc. (ERT), whose cooperation in providing SRI with monitoring data is gratefully acknowledged.

The monitoring network established for the SURE contains 54 stations covering a large area whose western boundary consists of all or parts of Minnesota, Iowa, Missouri, Arkansas, and Louisiana, and extends to the Eastern Seaboard. Nine of these stations, located in nonurban regions in eight states, monitored NO_x, NO, NO_2, and O_3, as well as other parameters. More details about the geographical and temporal coverage of the network and the experimental methods used will be given below.

The data base obtained in the SURE is unique because it is the most extensive set of observations collected in nonurban areas. By contrast, the majority of the data cited earlier in Tables 2 through 4 were obtained during special studies of short duration. Moreover, the SURE data were measured exclusively using the latest monitoring methods and, because the data are of recent vintage, portray better the contemporary air quality conditions that exist in nonurban areas of the United States. Consequently, this data resource merits analysis to supplement the data of Tables 2 through 4.

Before proceeding, it must be noted that the SURE data provided to SRI have undergone only preliminary validation by ERT, and have been released at this early date for purposes of scientific investigation only. We recognize that the data are preliminary, and assume full responsibility for any conclusions and interpretations that may be drawn from the data. We have closely scrutinized the data in the course of our analysis and have detected few inconsistencies; those data that appear to be spurious have been brought to the attention of ERT and have not been considered in the analysis.

B. Description of SURE Data

1. Geographical and Temporal Coverage

The geographical coverage of the monitoring network is displayed in Figure 3, which shows the locations of the nine sites. Table 11 lists the site names, their UTM coordinates, the cities nearest to each site, and any local sources that may affect pollutant levels at the site.

The continuous measurements run from August through December 1977. (The monitoring program will run through 1978, but only the August through December 1977 data were available for release when our study was undertaken.) The data consist of hourly averages of NO_x, NO, and O_3; NO_2 was estimated from the NO_x and NO data. The number of data points available for each parameter for each site is given in Table 12, which shows that the data capture rate (the percent of the maximum possible number of observations for which data are available) for NO_x ranges from 72 percent at Site 3 to 98 percent at Site 4. The data capture rate for NO varies from a low of 59 percent at Site 3 to 98 percent at Site 4. For O_3, the range of the data capture rate is from 82 percent at Site 3 to 99 percent at Site 6. Thus, except for NO at Site 3, the data set is quite complete.

Table 11

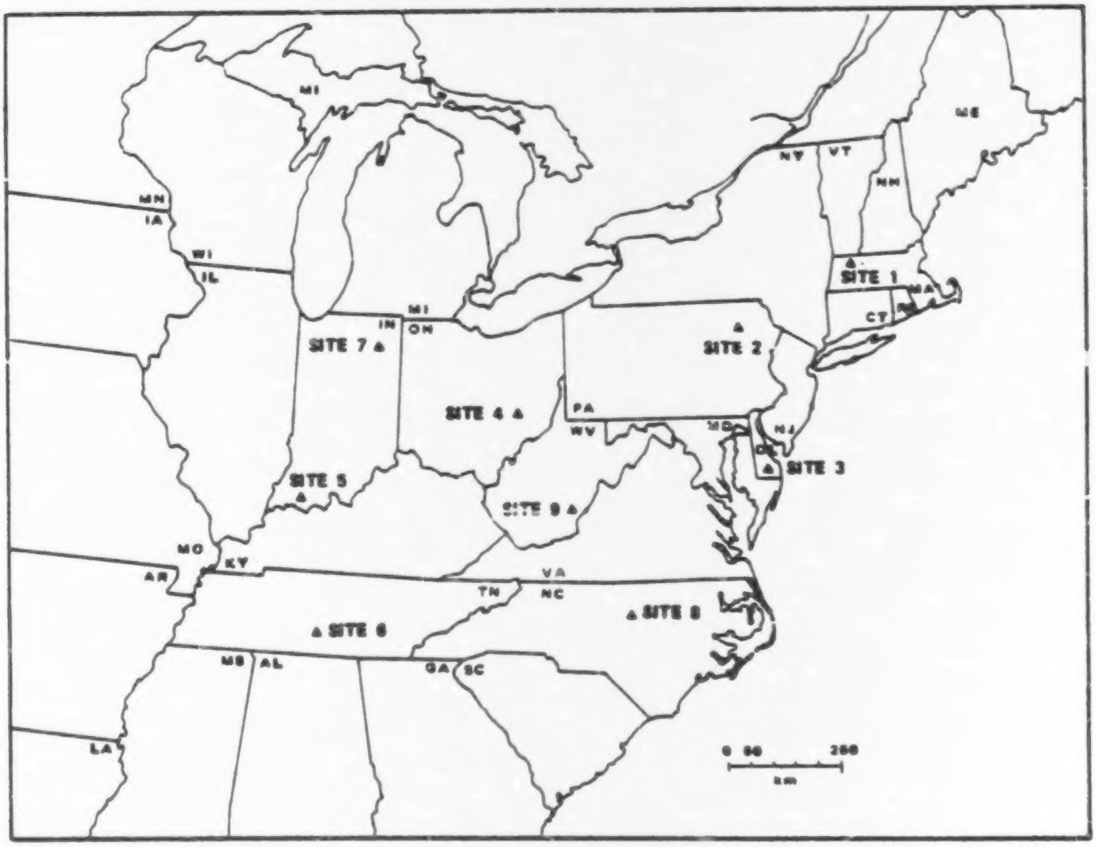
LOCATION OF MONITORING STATIONS IN THE SURE*

Station		UTM Coordinates (km)		UTM Zone	Nearest City	Miles†	Direction‡	Local Sources
No.	Name	X	Y					
01	Montague	702.88	4,715.55	18	Amherst, Massachusetts	15	N	
					Greenfield, Massachusetts	5	SE	
02	Scranton	410.64	4,604.80	18	Scranton, Pennsylvania	25	NW	Power plant 1 mi SE
03	Indian River	476.16	4,270.48	18	Millsboro, Delaware	1	E	Power plant 0.5 mi N
04	Duncan Falls	424.30	4,411.39	17	Zanesville, Ohio	8	SE	Metal processing plant 3.2 mi NE
05	Rockport	494.80	4,192.40	16	Rockport, Indiana	0.5	W	Power plants 8.5 mi S and 13.5 mi WNW
					Owensboro, Kentucky	8	N	Aluminum recycling plant 5 mi NE
06	Giles County	508.90	3,904.48	16	Columbia, Tennessee	24	SSE	
					Huntsville, Alabama	42	NE	
					Pulaski, Tennessee	10	NE	
07	Ft. Wayne	639.05	4,535.65	16	Ft. Wayne, Indiana	15	SW	Quarry (sant) 1.5 mi NE
08	Research Triangle Park	695.54	3,973.00	17	Durham, North Carolina	7	SE	Heavy traffic
					Raleigh, North Carolina	10	NW	
09	Lewisburg (Greenbrier Airport)	558.72	4,180.80	17	Lewisburg, West Virginia	5	E	
					White Sulfur Springs, West Virginia	2	SW	

[*] Adapted from Mueller et al. (1977).

[†] Distance between city and site.

[‡] Direction is from the city to the site.


MI
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SITE 3
SITE 5
SITE 9
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SITE 8
SITE 6
MS
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FIGURE 3 LOCATION OF SURE MONITORING STATIONS

Table 12

NUMBER OF AVAILABLE OBSERVATIONS
FOR SURE STATIONS
AUGUST-DECEMBER 1977

Site No.	NO_x*	NO*	O_3*
1	3330	3349	3419
2	2817	2814	3410
3	2629	2168	3017
4	3616	3616	3441
5	3408	3405	3462
6	3506	2415	3632
7	3216	3195	3438
8	3477	3482	3495
9	3303	3303	3459

*Each observation is an hourly average. Maximum possible number of observations is 3672.

2. Instrumentation

Table 13 shows the instruments used to measure the various compounds. The sensitivity limit of the NO_x and O_3 instruments is 2 ppb, based on manufacturer's specifications. A detailed discussion of the experimental methodology used in the SURE is given in Mueller et al. (1977).

C. Data Analysis

The analysis will first be concerned with establishing the character of each site, (i.e., suburban, rural, or remote), as revealed by the aerometric data. Although all the monitoring stations were carefully

Table 13

INSTRUMENTATION USED AT THE SURE SITES*

Parameter	Instrument	Method
NO, NO_x	Monitor Labs 8440	Chemiluminescent
O_3	Monitor Labs 8410	Chemiluminescent

*From Mueller et al. (1977), pp. 54 and 86.

located outside urban areas to maximize exposure to regional-scale phenomena, the sites are susceptible to some degree of influence from nearby sources, and this should be reflected in the data record. We will also analyze temporal and spatial concentration patterns, and will investigate relationships between the various pollutants.

A qualitative indication of the type of source affecting a site can be obtained from the daily cycle of concentration variations. Figures 4 through 12 display average diurnal curves for NO_x, NO, NO_2, and O_3 for Sites 1 through 9, respectively. Figures 5, 6, 8, 10, and 11 (respectively, Sites 2, 3, 5, 7, and 8) show evidence of influence from mobile source emissions. This influence is reflected in the plots of NO_x and NO, which have shapes typically associated with daily traffic patterns. A sign of mobile source influence is the presence of a morning NO_x peak, which mainly results from increased NO. Such a pattern is particularly strong in Figures 5, 6, and 11; it is weaker but still clear in Figures 8 and 10. The effect is especially pronounced at Site 8 (Figure 11), which is located in Research Triangle Park, North Carolina. This area contains a large U.S. Environmental Protection Agency laboratory and a sizable complex of private companies, but is outside the urban core. Hence, it reflects the influence of commuting patterns. Thus, Site 8 can be classified as suburban.

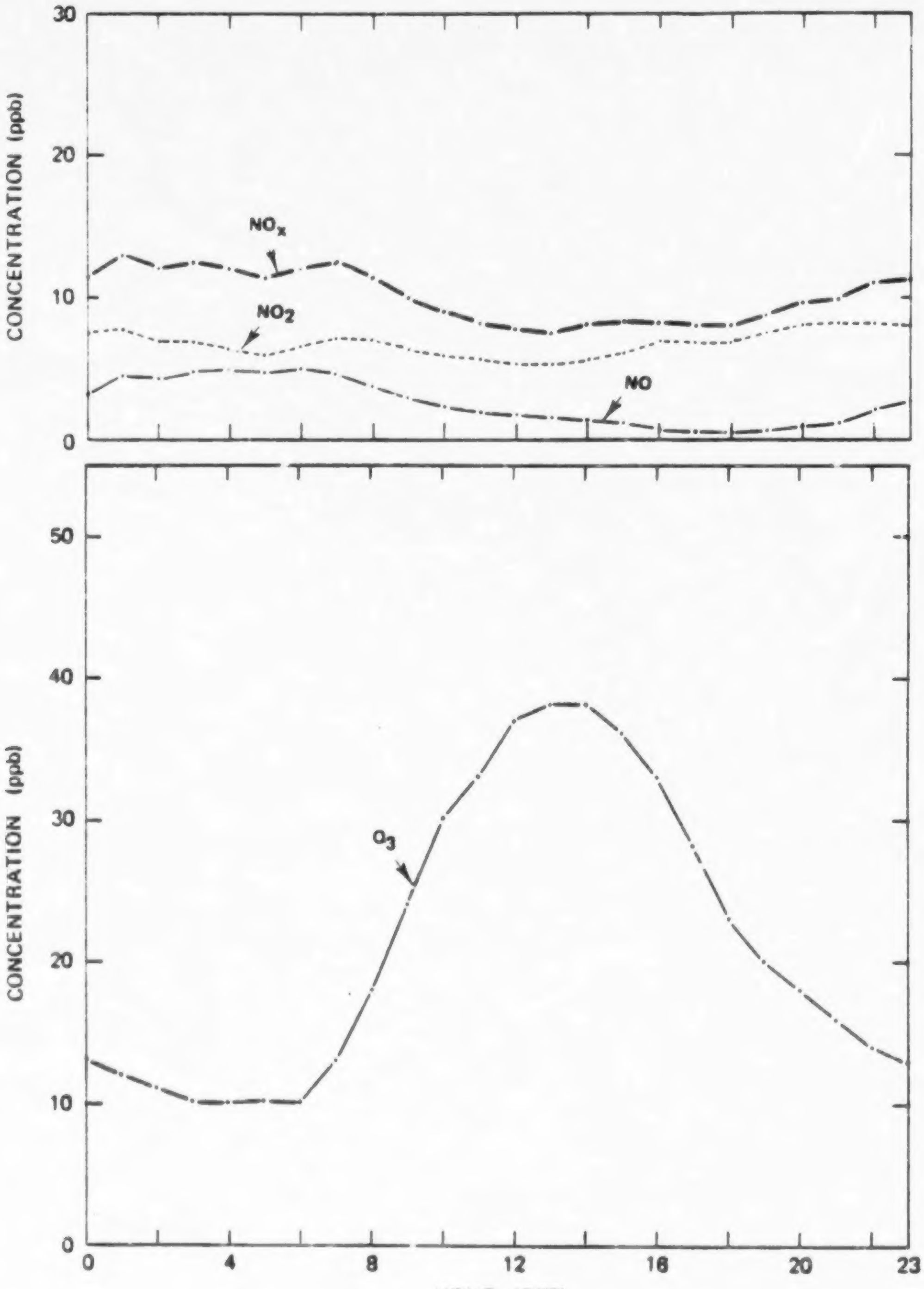

FIGURE 4 AVERAGE DIURNAL VARIATION OF NITROGEN OXIDES AND OZONE AT SURE SITE 1 IN MONTAGUE, MASSACHUSETTS, DURING AUGUST-DECEMBER 1977

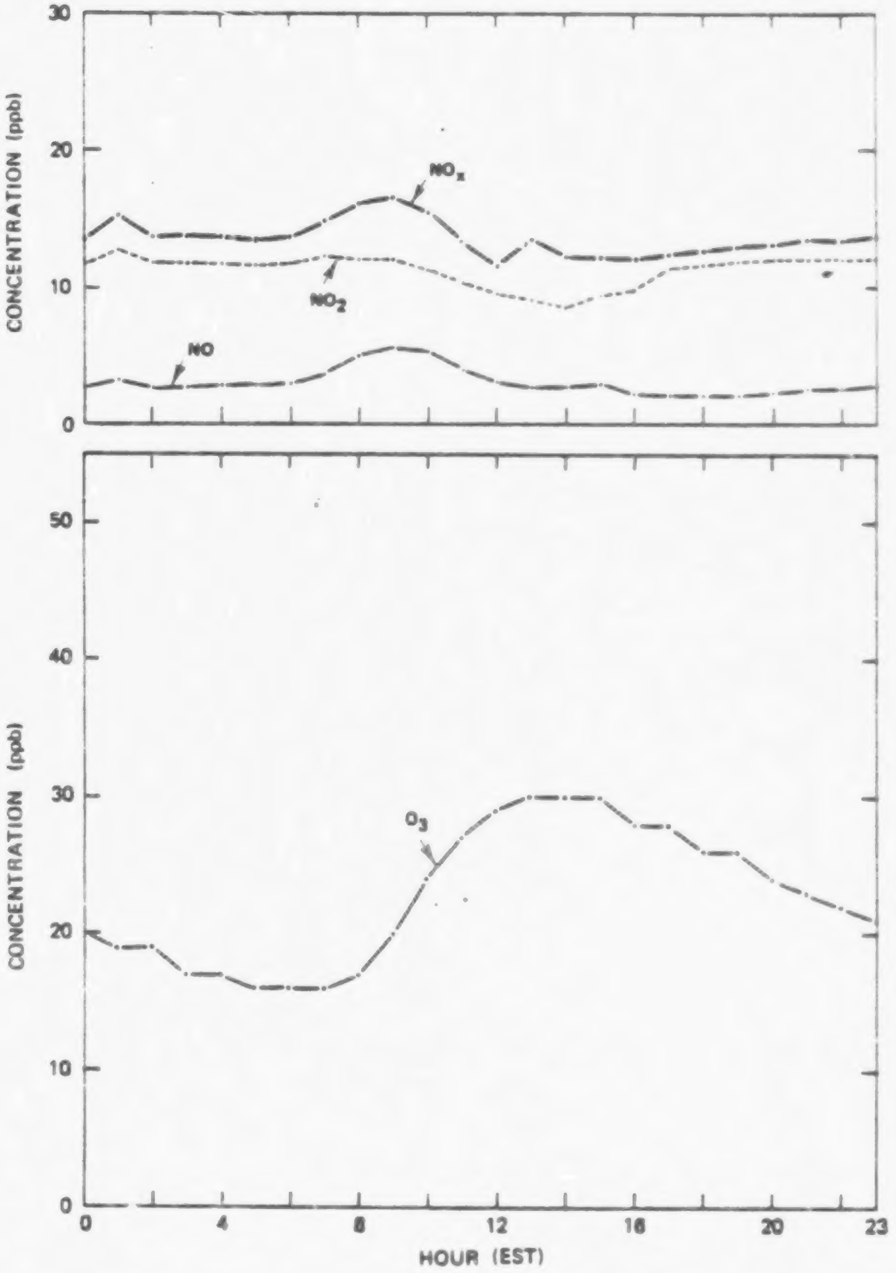

FIGURE 5 AVERAGE DIURNAL VARIATION OF NITROGEN OXIDES AND OZONE AT SURE SITE 2 IN SCRANTON, PENNSYLVANIA, DURING AUGUST-DECEMBER 1977

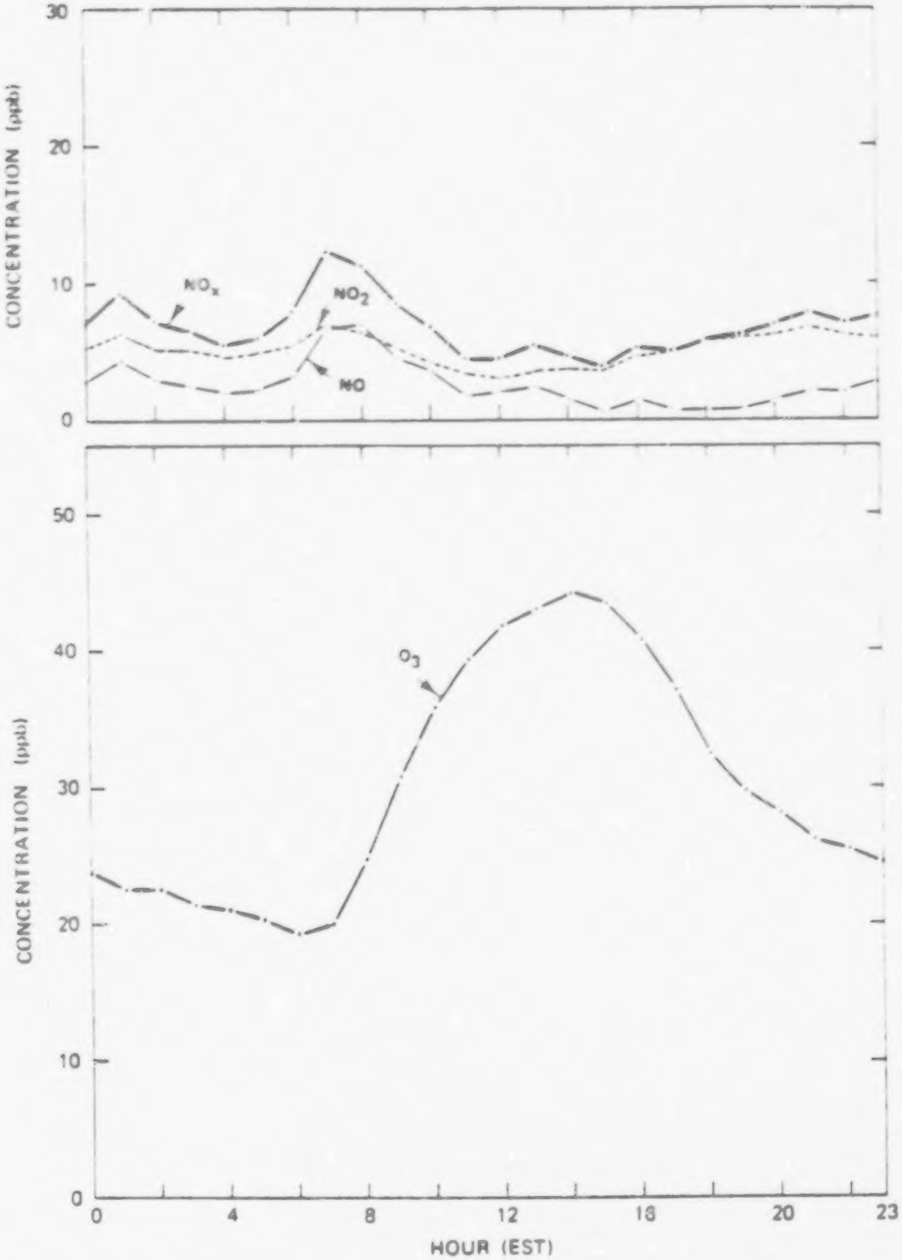

FIGURE 6 AVERAGE DIURNAL VARIATION OF NITROGEN OXIDES AND OZONE AT SURE SITE 3 IN INDIAN RIVER, DELAWARE, DURING AUGUST-DECEMBER 1977

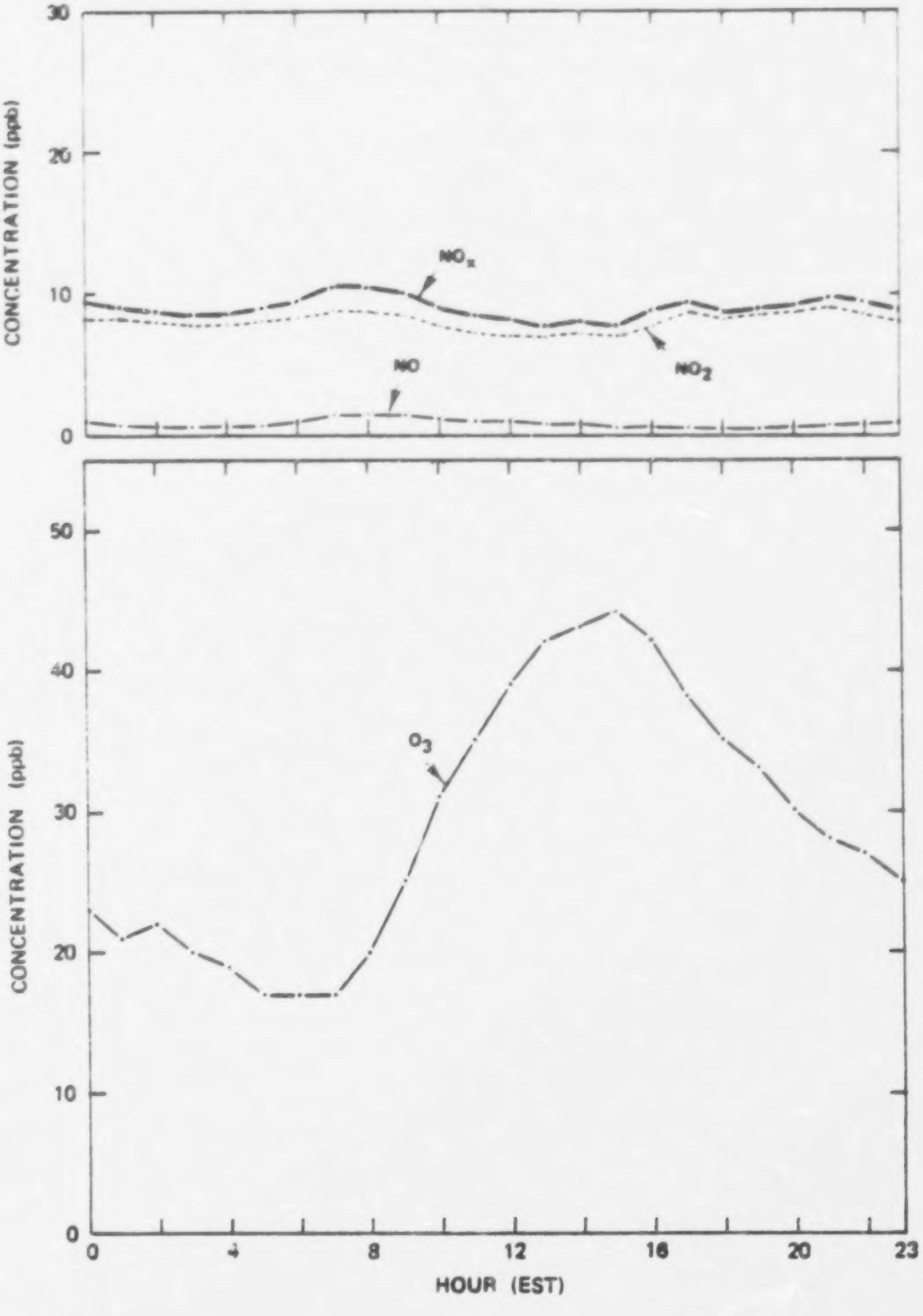

FIGURE 7 AVERAGE DIURNAL VARIATION OF NITROGEN OXIDES AND OZONE AT SURE SITE 4 IN DUNCAN FALLS, OHIO, DURING AUGUST-DECEMBER 1977

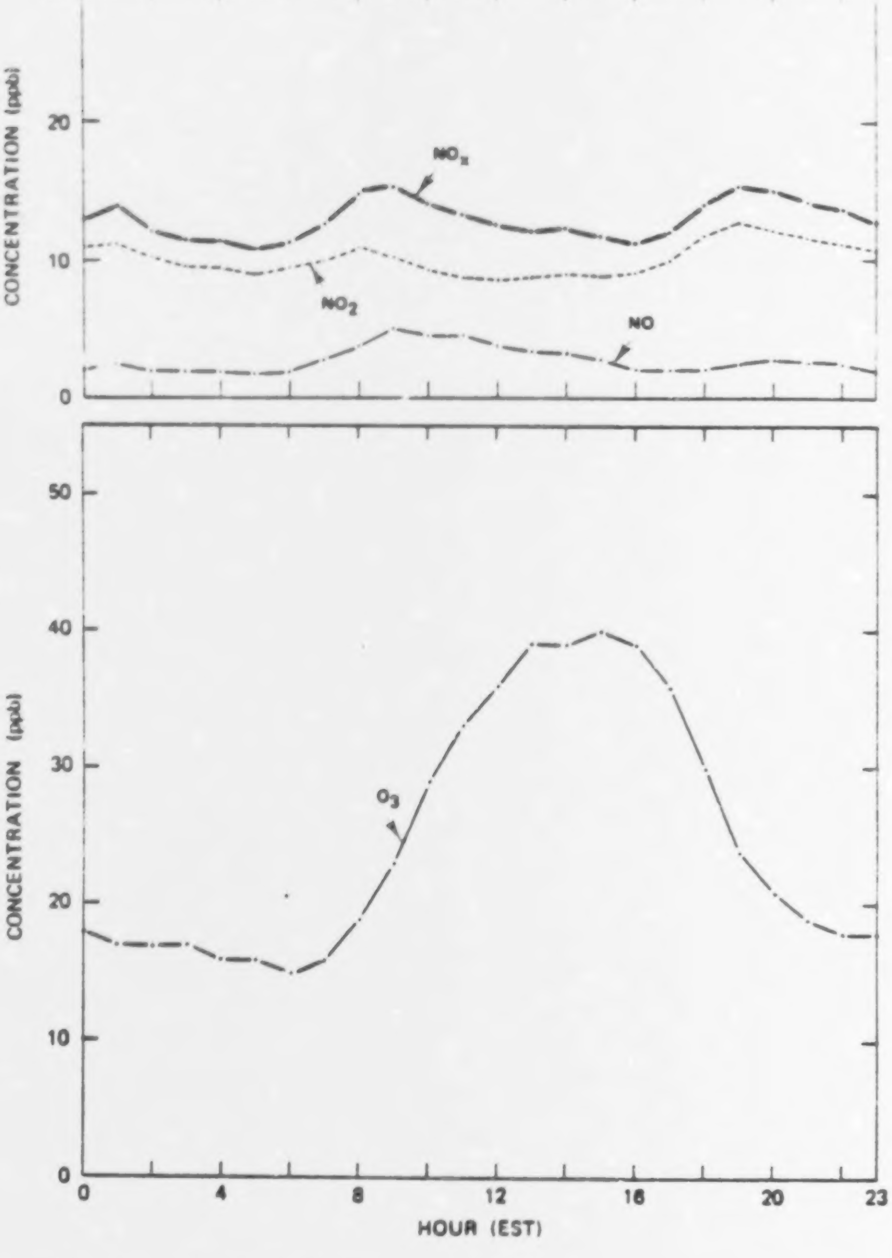

FIGURE 8 AVERAGE DIURNAL VARIATION OF NITROGEN OXIDES AND OZONE AT SURE SITE 5 IN ROCKPORT, INDIANA, DURING AUGUST-DECEMBER 1977

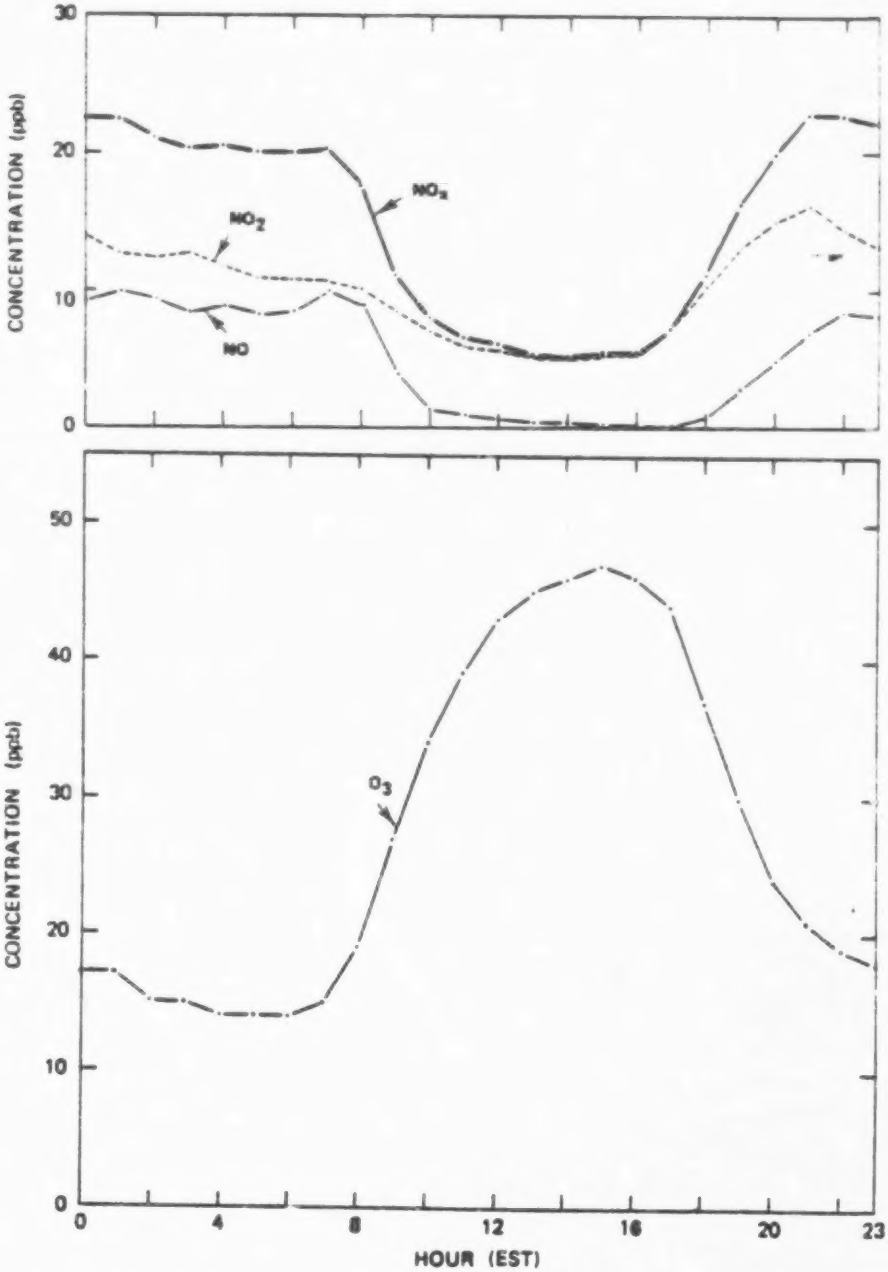

FIGURE 9 AVERAGE DIURNAL VARIATION OF NITROGEN OXIDES AND OZONE AT SURE SITE 6 IN GILES COUNTY, TENNESSEE, DURING AUGUST-DECEMBER 1977

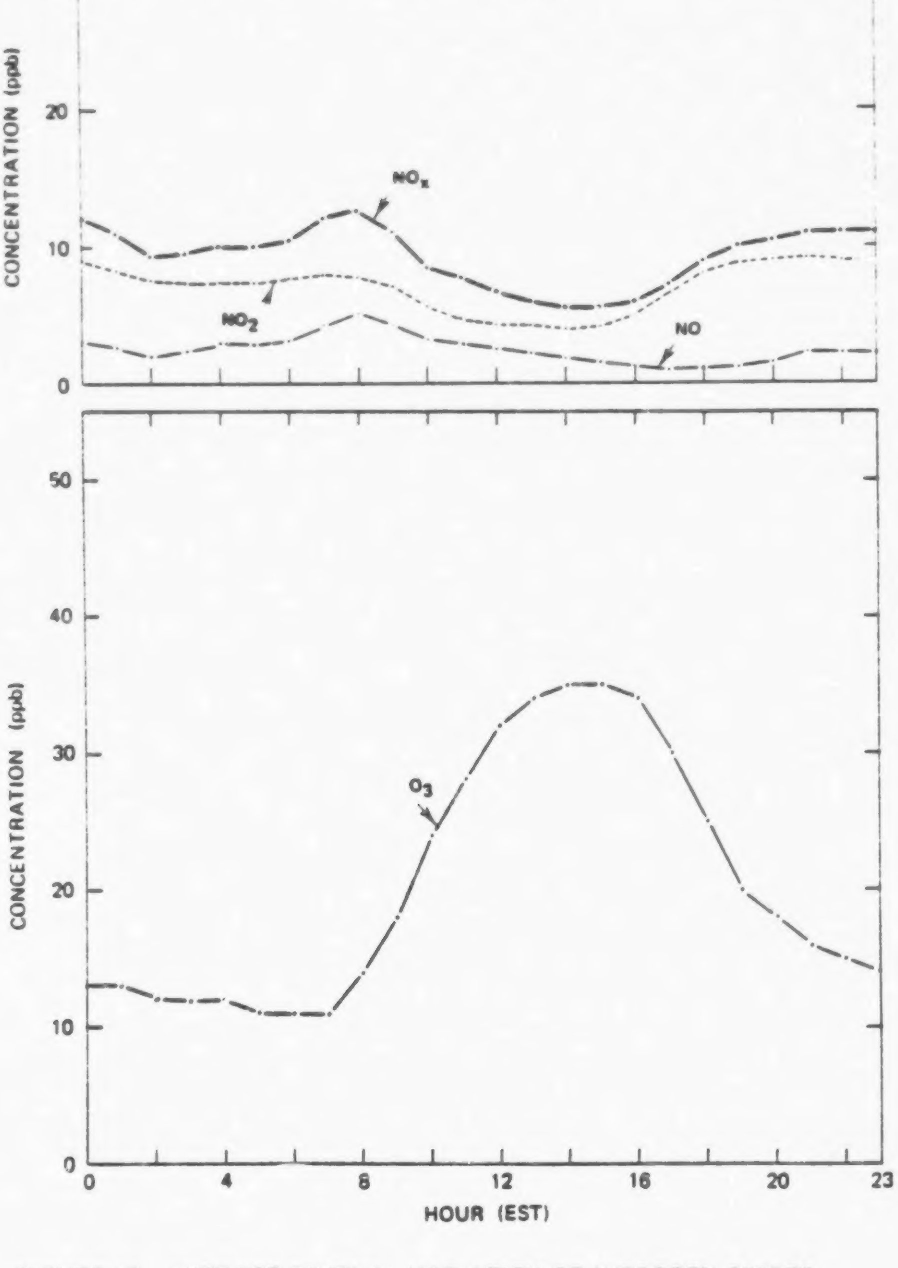

FIGURE 10 AVERAGE DIURNAL VARIATION OF NITROGEN OXIDES AND OZONE AT SURE SITE 7 IN FORT WAYNE, INDIANA, DURING AUGUST-DECEMBER 1977

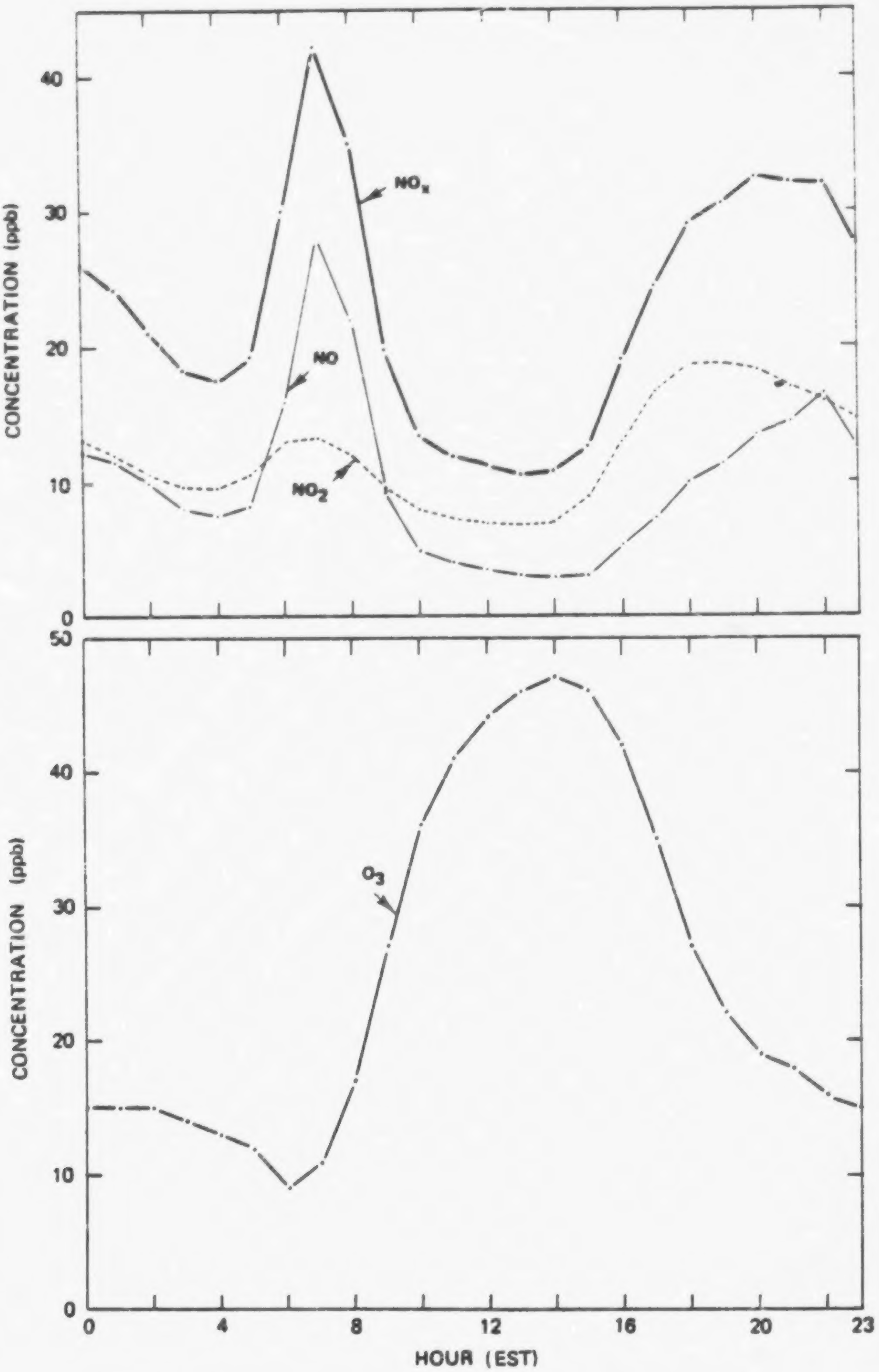

FIGURE 11 AVERAGE DIURNAL VARIATION OF NITROGEN OXIDES AND OZONE AT SURE SITE 8 IN RESEARCH TRIANGLE PARK, NORTH CAROLINA, DURING AUGUST-DECEMBER 1977

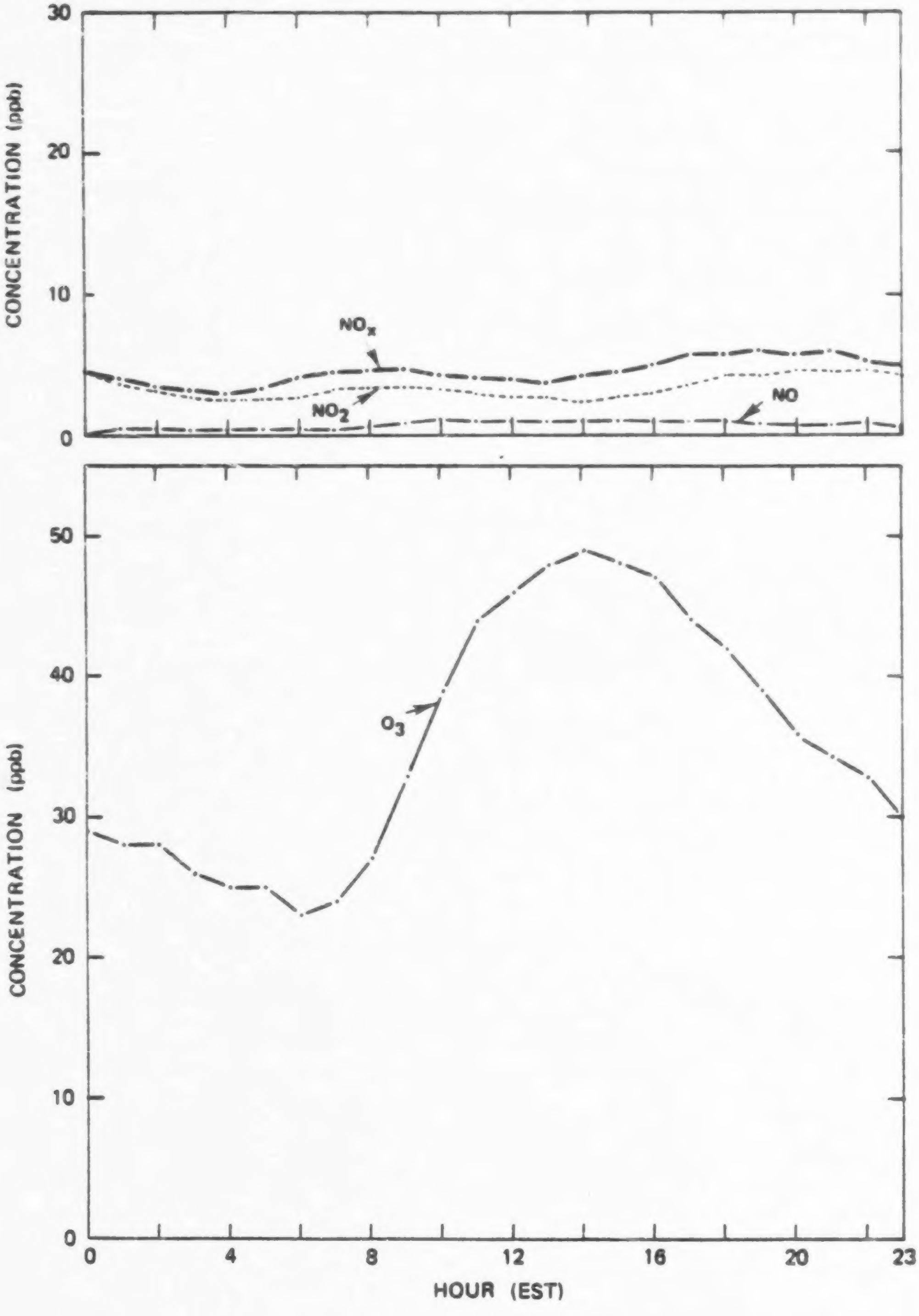

FIGURE 12 AVERAGE DIURNAL VARIATION OF NITROGEN OXIDES AND OZONE AT SURE SITE 9 IN LEWISBURG, WEST VIRGINIA, DURING AUGUST-DECEMBER 1977

At Sites 3 and 8 (Figures 6 and 11) the NO_x peak occurs about 0700, whereas it occurs later at Sites 2, 5, and 7 (Figures 5, 8, and 10). This suggests that Sites 3 and 8 are located close to the mobile sources, but that Sites 2, 5, and 7 are somewhat removed from the commuter traffic, yet feel its impact. Thus, it seems appropriate to classify Sites 2, 3, 5, and 7 as suburban.

Sites 1, 4, and 9 (Figures 4, 7, and 12, respectively) show no distinctive diurnal variations in nitrogen oxides; certainly nothing that resembles traffic-related concentrations. The essentially steady level of NO_x displayed at these sites suggests that, on the average, they are not particularly influenced by any one source. Thus, we conclude that regional-scale influences are the dominant factors at Sites 1, 4, and 9. Accordingly, these sites can be considered to be rural. The NO_x levels observed at these sites are such that none can be considered to be in the remote category.

The diurnal variation of NO_x at Site 6 displays a very slight NO peak at 0700, the NO decaying rapidly thereafter. This NO peak is largely reflected in the NO_x concentration, and it is probably not indicative of significant traffic influence. On the other hand, the nighttime levels of NO_x are second only to Site 8, which suggests considerable anthropogenic influence. The most probable cause is transport from urban areas, since there are no local sources nearby. Thus, Site 6 may be classified as a rural site that is a receptor for transported pollutants of urban origin.

Table 14 summarizes the data on nitrogen oxides and ozone at the nine sites. The table shows that, as might be expected, maximum NO levels are lower at rural sites than in the suburbs, except for Site 6. This is not the case for NO_2, however, some suburban sites having lower maxima than rural locations. The ozone maxima exceed 100 ppb at the four rural sites, but only at one of the five suburban locales (viz., Site 8).

Table 14

SUMMARY OF HOURLY CONCENTRATIONS OF NITROGEN OXIDES AND OZONE MEASURED AT THE SURE SITES DURING AUGUST-DECEMBER 1977

Site No.	Site Type	Maximum (ppb)*				Mean (ppb)				Mean Daily Maximum (ppb)			
		NO_x	NO	NO_2	O_3	NO_x	NO	NO_2	O_3	NO_x	NO	NO_2	O_3
1	Rural	109	78	73	153	10	3	7	21	24	11	16	44
2	Suburban	173	70	64	77	14	3	11	23	26	8	20	35
3	Suburban	151	114	48	99	7	3	5	30	29	17	17	49
4	Rural	94	53	43	107	9	1	8	29	21	4	18	49
5	Suburban	233	184	59	99	13	3	10	25	29	11	20	46
6	Rural	112	96	55	117	15	5	11	27	41	24	24	52
7	Suburban	101	99	35	80	9	3	7	20	24	14	15	39
8	Suburban	263	249	145	118	23	10	13	25	69	49	28	50
9	Rural	49	33	28	106	5	1	4	35	11	3	9	54

*Minimum value of all the species is zero at all sites.

It can be seen from Table 14 that mean values of NO are equal or lower at rural sites than at suburban locations. Once again, Site 6 is seen to be impacted by high NO levels, as evidenced by the mean. However, these high levels occur mostly at night, as shown in Figure 9. Mean NO_2 levels range from 4 to 13 ppb, and all the sites show comparable values. Mean ozone levels follow the same pattern as NO_2 except at Site 9, which shows both the lowest mean NO_2 and the highest mean ozone.

Because many concentrations are zero, the means are not necessarily the best indicators of pollutant levels at site. Thus, we use the mean daily maximum (MDM) as a descriptor of the ensemble of worst case conditions. Table 14 shows that for NO_x the MDM differs only slightly with location for Sites 1 through 5 and 7, with Sites 6, 8, and 9 differing substantially from the other sites. Site 8 has the highest MDM for NO_x, NO, and NO_2, and the third highest for O_3, whereas Site 9 shows the lowest MDM for the nitrogen compounds but the highest for ozone. Site 6 follows 8 in oxides of nitrogen, and resembles both 8 and 9 with respect to ozone. Thus, Site 9 is the "cleanest" in terms of NO_x, but contains significant amounts of O_3. Site 8 has the dubious distinction of being heavily polluted on all counts, as is Site 6. However, these data for Site 6 can be misleading, since the NO_x maxima are a nighttime phenomenon, whereas this is not the case at Sites 8 and 9. It appears that Site 9 is a receptor of aged pollutant plumes, while at Site 6 local ozone synthesis predominates, the precursors having been transported or otherwise retained overnight. At Site 8, it is likely that a significant fraction of the secondary pollutants is locally produced, thereby adding to the pollution transported from the surrounding urban areas.

It should be noted that almost half of the oxides of nitrogen data for Site 3 consist of zeros. This may be an indication of data problems, and Site 3 data should be treated with caution. The preponderance of zeros will tend to lower the means of NO_x, NO, and NO_2 shown in Table 14, which is why mean NO_x is lower at Site 3 than at any other station except Site 9. No other site exhibits as large a fraction of zeros in the NO_x data as does Site 3.

It is of interest to examine the NO/NO_x ratio at the various sites, as it provides some insight regarding the presence of unreacted NO. Thus, as was seen in Section II-C, one expects a high NO/NO_x ratio in urban and suburban areas, and lower ratios in rural and remote locations. Table 15 lists the ratio of mean NO to mean NO_x for the various sites.

Table 15

NO/NO_x RATIOS FOR THE SURE SITES
AUGUST-DECEMBER 1977

Site No.	NO/NO_x
1	0.30
2	0.21
3	0.43
4	0.11
5	0.23
6	0.33
7	0.33
8	0.43
9	0.20

Table 15 shows that Sites 4 and 9, two rural sites, have the lowest ratios, as expected. However, Sites 1 and 6, which are also rural, have ratios that are closer to those exhibited by the suburban stations. On this basis, it appears that Sites 1 and 6 may be transitional suburban-rural locations. Sites 2, 5, and 7 also seem to be hybrid suburban-rural locations, since their respective NO/NO_x ratios are lower or equal to the ratios at Sites 1 and 6. However, as previously noted, the hourly fluctuations of NO and NO_x at Sites 2, 5, and 7 indicate the presence of local mobile sources (cf. Figures 5, 8, and 10), which was the reason for classifying them as suburban instead of rural. Sites 3 and 8 show the highest ratios, further indication of the heavy impact of mobile sources at these two locations.

Ozone concentrations greater than 80 ppb occurred infrequently or not at all at the various sites. Table 16 shows the number of hours when O_3 exceeded 80 and 100 ppb at each monitoring station. Exceedances of 80 ppb range from zero at Sites 2 and 7 to a maximum of 81 hours at Site 8. The 100 ppb threshold was surpassed at Sites 1, 4, 6, 8, and 9. All the high O_3 concentrations were recorded during August-October. One concentration of 82 ppb was observed at 1500 on 16 November at Site 3.

It is apparent from Table 16 that Site 1 exhibits the largest number of exceedances of 100 ppb. The other rural sites, Sites 4, 6, and 9, also show several instances when ozone surpassed 100 ppb, but the frequency is much lower than at Site 1. Thus Site 1 is subject to influences that differ qualitatively from those affecting the other rural stations.

Site 8 has the highest number of exceedances of 80 ppb, but relatively few of those exceed 100 ppb. The probable cause of this phenomenon is that the preponderance of NO at this site (the NO/NO_x ratio is 0.43, cf. Table 15) tends to reduce the maximum level that ozone can reach. Moreover, as will be seen shortly, exceedances of 100 ppb at Site 8 tend to occur late in the day, and thus are likely to be associated with transport from surrounding areas.

Table 16 shows that the new ozone standard of 120 ppb was exceeded only at Site 1. The number of exceedances of the standard recorded at Site 1 was 21, with ozone levels ranging from 121 to 153 ppb. Below we investigate these events in detail.

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Table 16

NUMBER OF HOURS WITH OZONE CONCENTRATIONS EXCEEDING 80, 100, AND 120 ppb AT SURE SITES AUGUST-DECEMBER 1977

Site No.	Total Hours Observed	Number of Hours O_3 > 80 ppb	Number of Hours O_3 > 100 ppb	Number of Hours O_3 > 120 ppb	Maximum Hourly O_3 Concentration (ppb)
1	3419	60	33	21	155
2	3410	0	0	0	77
3	3017	29	0	0	99
4	3441	52	2	0	107
5	3462	17	0	0	99
6	3632	63	5	0	117
7	3438	0	0	0	80
8	3495	80	10	0	118
9	3459	23	3	0	106

It is noteworthy that Sites 1, 4, 6, and 9, which are considered to be rural, account for a sizable fraction of the exceedances of 80 ppb. Nevertheless, in comparison to urban areas, these sites (indeed, all the sites) are relatively clean with respect to ozone. Thus, although ozone maxima reach levels comparable to those found in urban areas, the frequency of occurrence of these high values is quite low. This suggests that local ozone generation is probably not a main contributor to elevated ozone concentrations. Instead, the low frequencies associated with high ozone values may indicate that an infrequent event such as the wind blowing from a specific direction is required to increase ozone beyond 80 or 100 ppb.

Those days when the hourly ozone maximum exceeded 100 ppb will be investigated below in a series of case studies. The case studies include descriptions of prevailing meteorological conditions and trajectory analyses. It would have been useful to examine ozone levels recorded in neighboring communities on these occasions. However, we were unable to do so because of constraints of time and data availability.

The maximum daily ozone exceeded 100 ppb on 16 days at four sites. The exceedances are listed in Table 17 by site, together with the time of occurrence of the peak. The table shows that Sites 1 and 8 accounted for 11 of the 16 high-ozone days. Except as detailed below, all the maxima are single-day events.

Site 1 appears to have experienced a three-day episode during 3-5 August, a maximum concentration of 97 ppb on 3 August (not shown in Table 17) having preceded the peaks for 4 and 5 August listed in Table 17. The 3 August peak occurred at 1500 local time. Another three-day episode may have taken place in the period 27-29 August at this site.

The 9 August maximum of 109 ppb at Site 8 was preceded by a peak of 83 ppb on 8 August, and was followed by maxima of 87 and 90 ppb on 10 and 11 August, respectively. This suggests a moderate four-day episode. Similarly, at Site 9, the peak on 22 October was followed by maximum

Table 17

OCCURRENCE OF MAXIMUM DAILY OZONE EXCEEDING 100 ppb AT THE SURE SITES DURING AUGUST-DECEMBER 1977

Site No.	Date	Day of Week	O_3 Concentration (ppb)	Time of Occurrence (Local Time)
1	4 Aug	Thu	139	1700
1	5 Aug	Fri	142	1300
1	27 Aug	Sat	147	1800
1	28 Aug	Sun	153	2000
1	29 Aug	Mon	140	1300
1	1 Sep	Thu	102	1700
4	2 Sep	Fri	107	1300
6	2 Aug	Tue	115	1900
6	22 Aug	Mon	101	1300
6	23 Sep	Fri	117	1500
8	9 Aug	Tue	109	1700
8	26 Aug	Fri	106	1600
8	31 Aug	Wed	118	1500
8	10 Sep	Sat	102	1600
8	23 Sep	Fri	115	1700
9	22 Oct	Sat	106	1600

levels of 88 and 87 ppb on 23-24 October, which could be evidence of a three-day episode. Likewise, the peak of 2 September at Site 4 was bracketed by a maximum of 85 ppb on the previous day, and peaks of 74, 91, and 87 ppb on the three days immediately following.

The ozone peak of 115 ppb observed at Site 6 on 2 August was bracketed by maxima of 86 and 80 ppb on 1 and 3 August, respectively, which suggests a mild three-day episode. A four-day interval of high ozone levels occurred during 21-24 August. In this period, the 101 ppb maximum of 22 August was preceded by a peak of 88 ppb on 21 August, and followed by two consecutive days with peaks of 94 and 95 ppb, respectively.

Note that all the rural sites (viz., 1, 4, 6, and 9) appear in Table 17. The relatively late time of occurrence of most of the ozone peaks at these sites suggests that, on these days at least, transport is the primary contributor to oxidant pollution at the rural locations. The influence of transport is also evident at Site 8. Thus, the high-ozone events may yield some clues about the effect of transport on oxidant pollution in outlying areas. Case studies of these high-ozone days are provided below.

1. Case Study I: High-Ozone Events at Montague, Massachusetts (Site 1)

Figures 13 through 19 display pollutant histories for the high-ozone days at Site 1. Figures 13 through 15 depict the three-day episode that occurred during 3-5 August, and Figures 16 through 18 portray a similar incident occurring on 27-29 August. Figure 19 illustrates the single-day event of 1 September.

Analysis of surface weather data revealed that on 3 August a low pressure front had recently passed over New England, and that moderate high pressure prevailed in the Northeast. The high-pressure system remained over the area on 4 and 5 August, being replaced by low pressure and precipitation over New York, Massachusetts, and other parts of New England. Thus, the classic meteorological elements of an air pollution episode prevailed during 3-5 August 1977. A similar situation occurred on 27-29 August, except that the high-pressure system was already well established by 26 August, and spread from North Carolina to Maine. No significant precipitation was reported during this period, but a cold front that spread rain over a large area was approaching on 29 August. It passed over the area on 30 August, ending the episode. A high-pressure system was reestablished by 31 August, and remained over the area through 1 September.

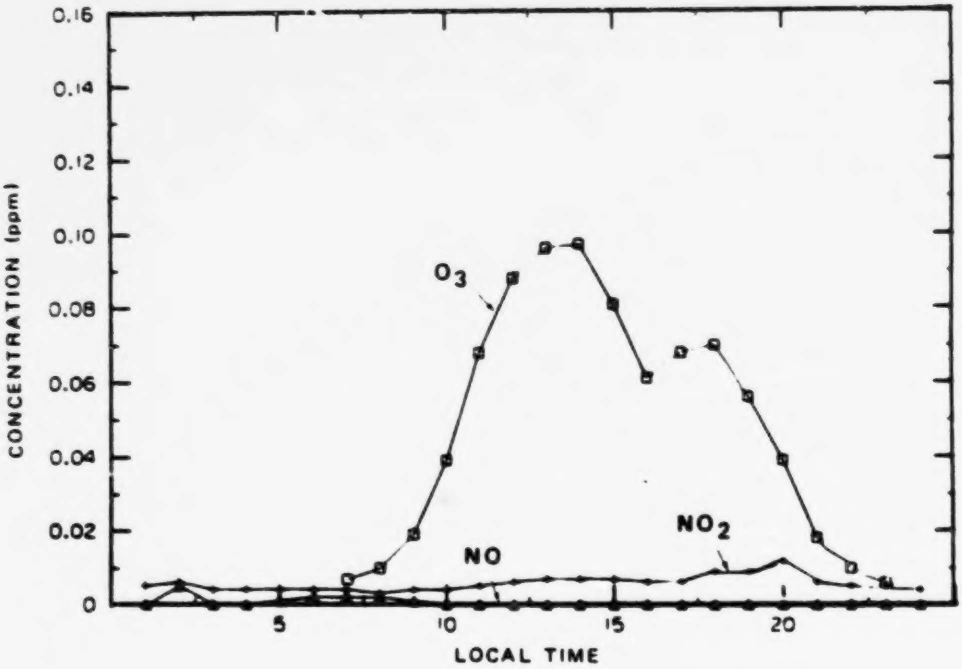

FIGURE 13 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 1 ON WEDNESDAY, 3 AUGUST 1977

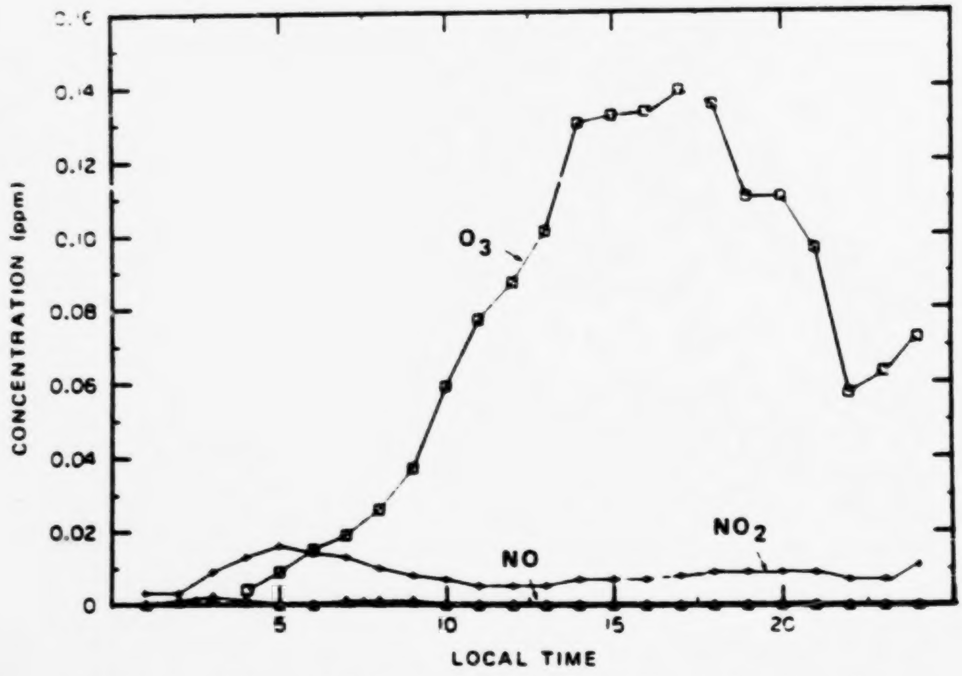

FIGURE 14 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 1 ON THURSDAY, 4 AUGUST 1977

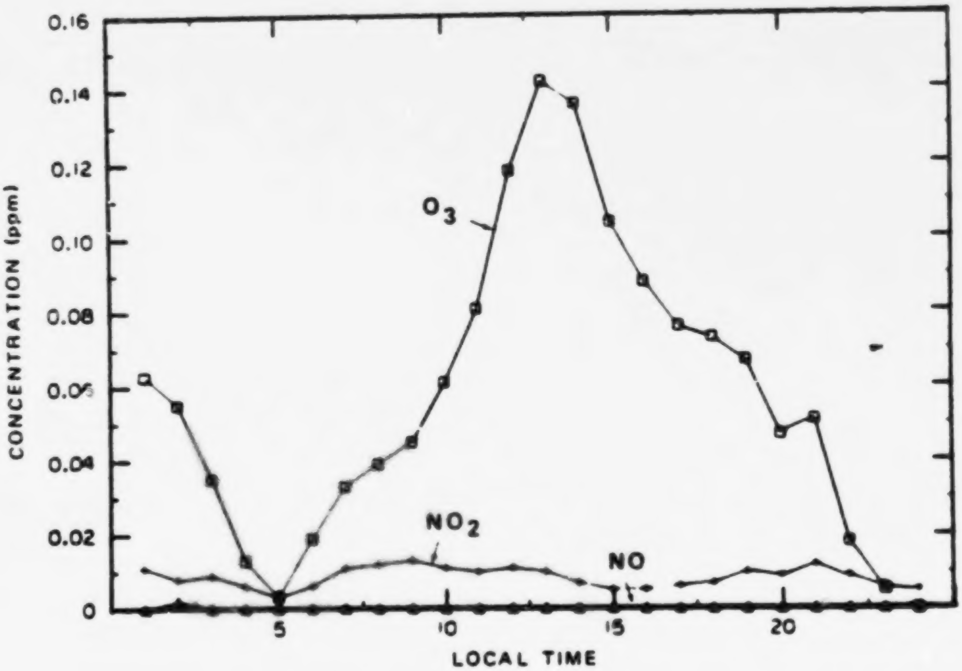

FIGURE 15 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 1 ON FRIDAY, 5 AUGUST 1977

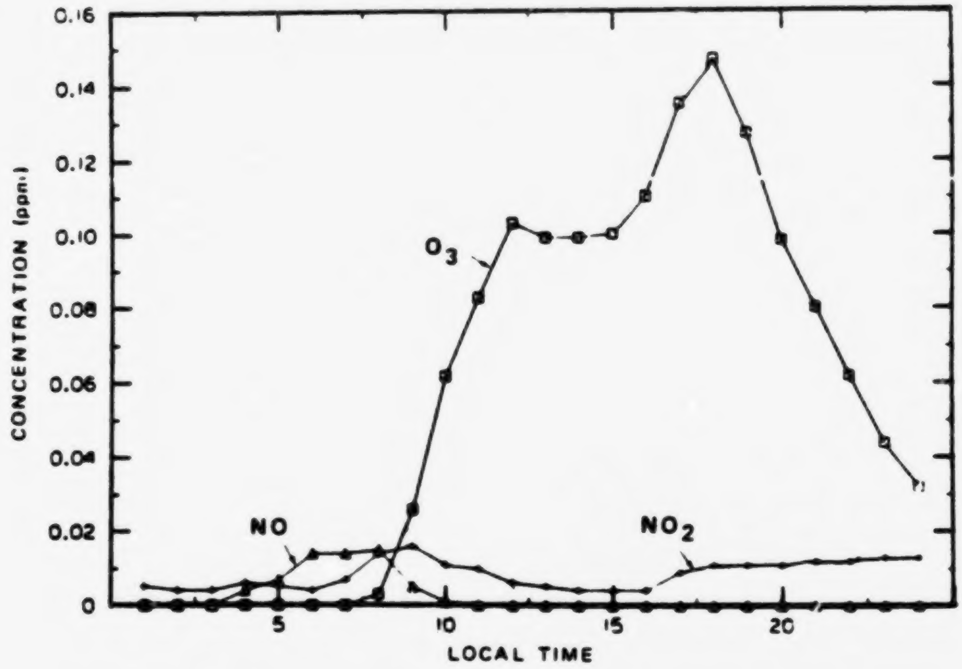

FIGURE 16 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 1 ON SUNDAY, 28 AUGUST 1977

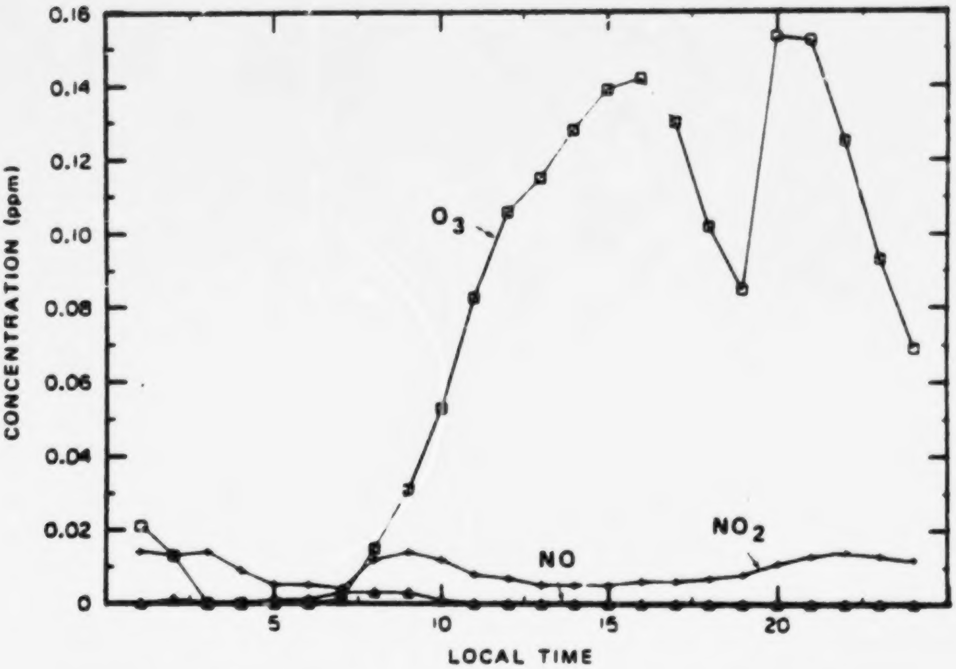

FIGURE 17 HOURLY CONCENTRATION VARIATIONS OF NO, NO$_2$, AND O$_3$ AT SITE 1 ON SUNDAY, 28 AUGUST 1977

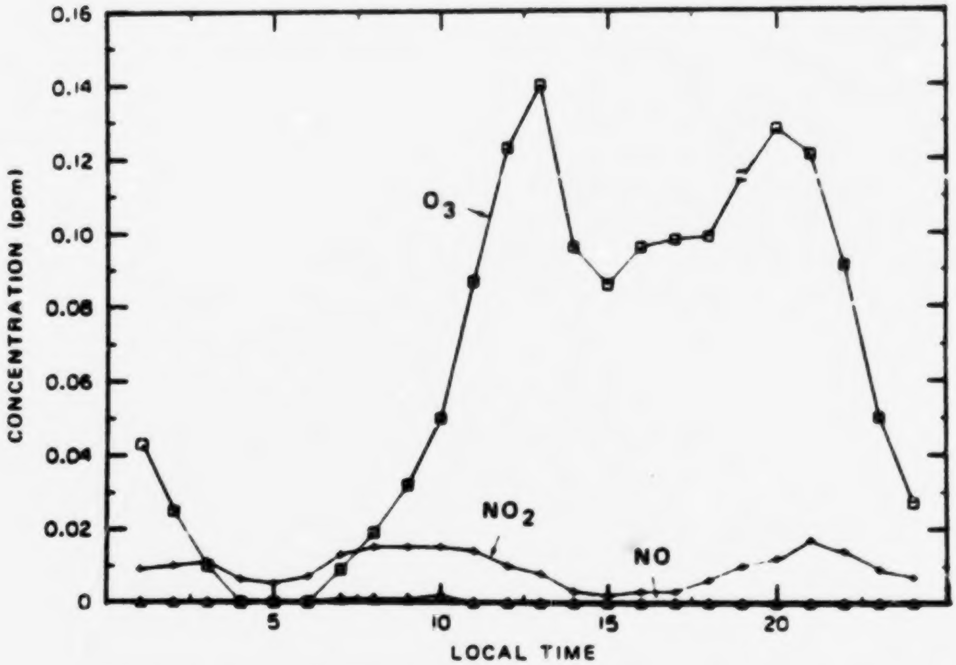

FIGURE 18 HOURLY CONCENTRATION VARIATIONS OF NO, NO$_2$ AND O$_3$ AT SITE 1 ON MONDAY, 29 AUGUST 1977

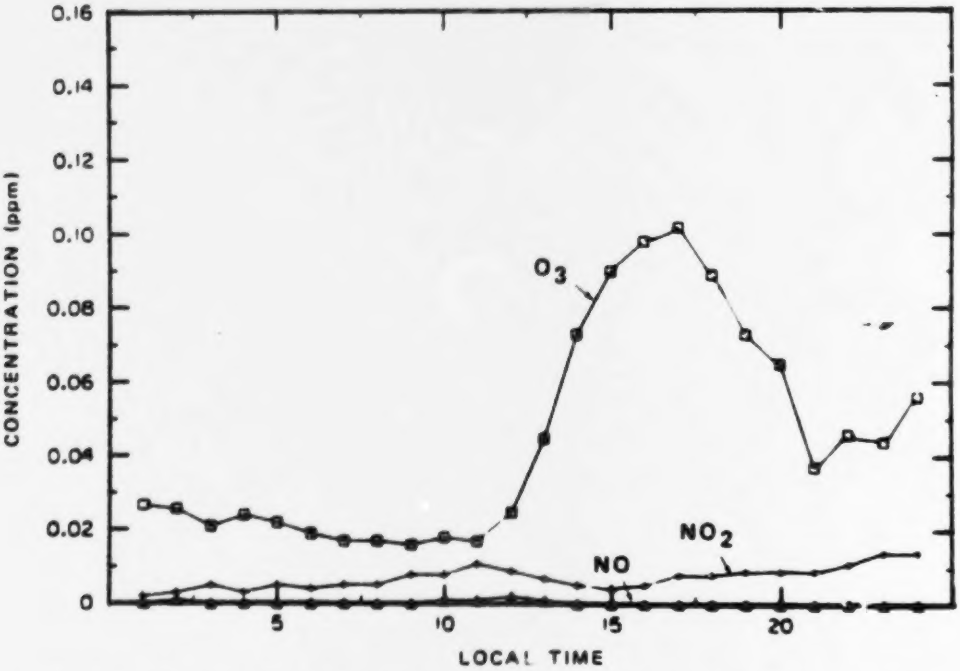

FIGURE 19 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 1 ON THURSDAY, 1 SEPTEMBER 1977

A striking feature of Figures 13 and 16 through 18 is the presence of a double peak in the ozone curve. This phenomenon is often observed at locations impacted by pollutants transported from other areas. The first ozone peak is generally associated with local photochemical activity and the second, which occurs in the late afternoon or in the evening, is attributed to transport. The figures show that the two ozone peaks are separated by four to seven hours. In Figure 13, the first peak has a magnitude of 97 ppb and occurred at 1400; the second occurs at 1800 and its magnitude is 70 ppb. The second peak is higher than the first in Figures 16 and 17, but not in Figure 18. Six hours separate the two peaks on 27 August (Figure 16), increasing to seven hours on 29 August (Figure 18). The difference is only four hours on 3 and 28 August (Figures 13 and 17). In all four cases, the second ozone peak is accompanied by slight but noticeable increases in NO_2. Levels of NO at the time of the second peak on all four days are less than 1 ppb, which is below the minimum level of detectability of the instrument.

The ozone buildup during the episode of 3 to 5 August is shown in Figures 13 through 15. Ozone concentrations remain rather high until about 2000 on 3 August, and NO_2 levels increase during the day and early evening, peaking at 2000. However, there is little or no ozone carry-over into the next day. Ozone begins to accumulate very early in the morning of 4 August, the accumulation being preceded by a buildup of NO_2, which is almost certainly due to transport. NO_2 peaks at 0500, and decays slowly but steadily on 4 August until about 1000, remaining essentially constant thereafter. Meanwhile, ozone reaches a late peak of 139 ppb at 1700. Afterwards, ozone remains high until about 0200 on 5 August, when it decays rapidly. The accumulation of ozone begins again after 0500 on 5 August, reaching a peak at 1300, decaying quickly thereafter. NO levels are very low throughout the whole episode.

Figures 20 through 22 show estimated trajectories arriving at Site 1 during 3 to 5 August 1977. Each figure contains at most four individual trajectories which arrive at 0200, 0800, 1400, and 2000 (local time). The trajectories were computed using a procedure devised by Heffter and Taylor (1975). The nodes of each trajectory are separated by six hours.

The trajectories for 3 August are depicted in Figure 20. The air arriving at 0200 and 0800 originated in southern Canada and has passed over areas of precipitation on its way to Site 1. Consequently, it is probably relatively clean. By 1400, the path has shifted, the air passing over industrialized areas of Pennsylvania and New York before arrival, essentially the same track being followed by the air arriving at 2000. It is interesting that these two trajectories coincide respectively with the ozone maximum at 1400 and a peak in NO_2 at 2000. Since the 1400 and 2000 trajectories coincide, it is probable that between

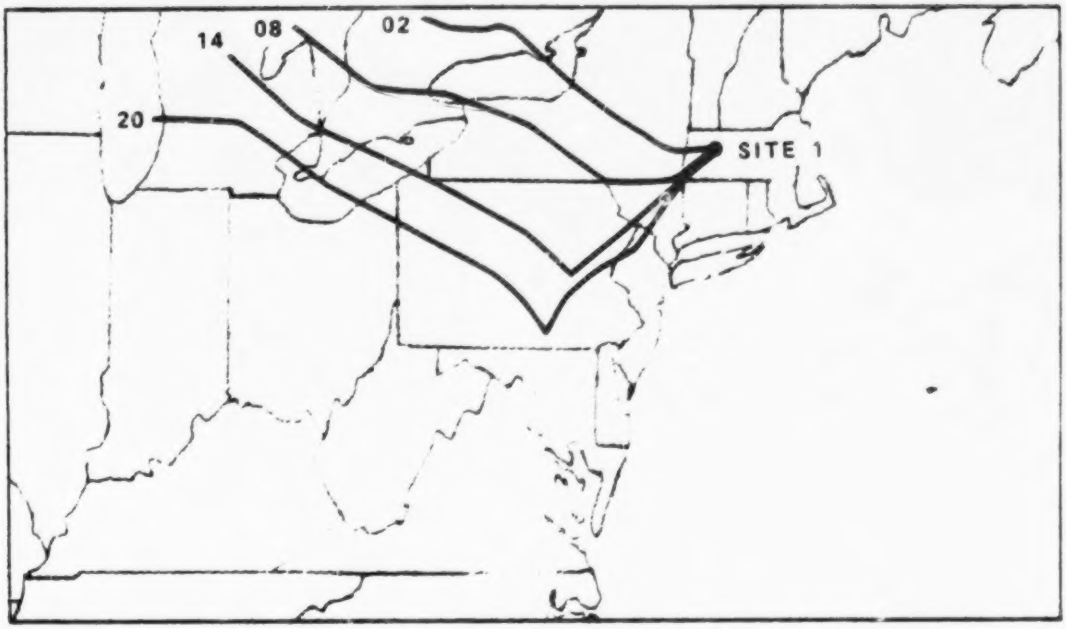

FIGURE 20 TRAJECTORIES ARRIVING AT SITE 1, MONTAGUE, MASSACHUSETTS, ON 3 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

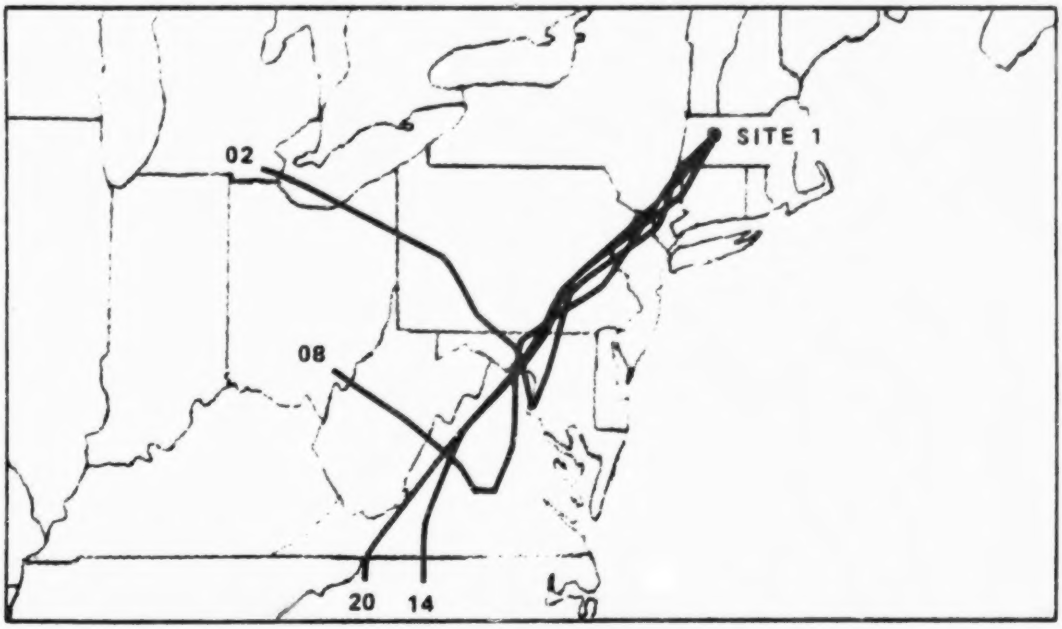

FIGURE 21 TRAJECTORIES ARRIVING AT SITE 1, MONTAGUE, MASSACHUSETTS, ON 4 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

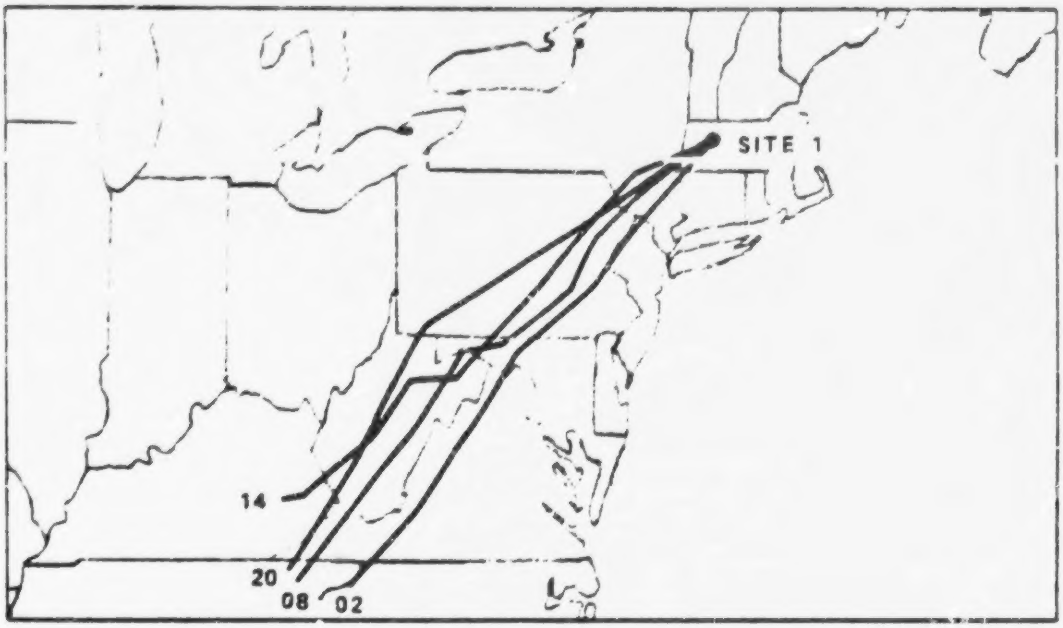

FIGURE 22 TRAJECTORIES ARRIVING AT SITE 1, MONTAGUE, MASSACHUSETTS, ON 5 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

1400 and 2000 the air continued to pass over the same pollution sources, which may be responsible for the ozone increase between 1600 and 1800.

The pattern of air movement seen in the afternoon and evening of 3 August is essentially repeated on 4 and 5 August, as shown in Figures 21 and 22, respectively. The air flows from a southwesterly direction into the site, passing over southeastern Pennsylvania and the southern tip of New York along the way. These air masses originated entirely within a high-pressure system with its attendant reduction in the ability to disperse pollutants. Thus, it is highly probable that on 4 August the air masses could accumulate high pollutant levels, which were transported to the site. This process continues through the night of 4 August, and is likely responsible for the carryover of O_3 and NO_2 into 5 August. From the larger spacing between the nodes of the trajectories for 5 August (cf. Figure 22), it can be inferred that the wind speed of the 1400 and 2000 trajectories has increased, which may explain the afternoon drop in ozone concentration on 5 August (cf. Figure 15).

The above discussion suggests that it is very likely that transport is responsible for the ozone levels observed on 3 and 4 August. Although the ozone maximum occurred at 1300 on 5 August, it does not appear likely that it is due to local chemical activity. The reason is that NO and NO_2 change very little throughout the day, which tends to discount the possibility that local precursors are responsible for the ozone. In fact, the prevailing very low level of NO and the concomitant high NO_2/NO ratio suggest that the ozone was formed on the way to the site. Thus, it is probable that transport is responsible for the ozone peak. A potential contributing factor to the total ozone burden at Site 1 on 5 August is ozone fumigation that accompanies the breakup of a nocturnal radiation inversion. Analysis of three-hour surface weather maps indicated that a ground-based inversion was present in the early morning of 5 August. This is consistent with the fast decay of ozone levels that occurs between midnight and 0500, since such a rapid change is associated with gas-phase and surface reactions that deplete the ozone present in a shallow mixed layer. The weather data also show that the inversion has lifted by about 1000, which suggests that the ozone increase up to that time may result from downward transport of ozone stored aloft. (Note that the ozone concentration at 1000 matches that previously measured at midnight.) In view of the very light to calm wind conditions that prevail in the area, the level of ozone present at midnight can be interpreted as an indication of the concentration of ozone stored aloft. If so, this concentration will be restored upon lifting of the inversion, which is precisely what happens by 1000. Thus, downward ozone transport may have contributed up to 60 ppb during the early stages of the ozone buildup.

Data on pollutant levels are given in Table 18 for the high ozone days at Site 1. The table and the plots show that the level of NO

Table 18

DATA SUMMARY FOR HIGH-OZONE DAYS
AT SURE SITE 1 IN 1977

Date	Mean O_3 (ppb)	Mean NO_2 (ppb)	Mean NO (ppb)	Maximum O_3 (ppb)	Time of Occurrence of Maximum (Local Time)
3 Aug	49	6	<1	97	1400
4 Aug	77	8	<1	139	1700
5 Aug	57	8	<1	142	1300
27 Aug	59	8	<1	147	1800
28 Aug	73	9	<1	153	2000
29 Aug	64	9	<1	140	1300
1 Sep	44	7	<1	102	1700

for the high ozone days is very low. Comparing the mean NO level from Table 18 with the five-month mean of 3 ppb for Site 1 (cf. Table 14) shows that although this site usually experiences NO concentrations greater than 1 ppb, on high-ozone days essentially all the NO has been converted to NO_2 thereby enhancing net ozone production. Table 18 By contrast, mean NO_2 levels on all high ozone days range from 6 to 9 ppb, and are comparable to the five-month mean of 7 ppb. Thus, NO_2 levels are only slightly affected on these high-ozone days, which is further indication that high concentrations of ozone are probably due to transport, rather than to local influences.

The episode of 27-29 August exhibits the double ozone-peak phenomenon on all three days. The second peak undoubtedly results from the arrival of an aged air mass loaded with pollutants. As Figures 16 through 18 show, these late ozone peaks are accompanied by increases in NO_2 but not in NO, which would be expected in an air mass that has converted essentially all the NO to NO_2. The occurrence of the late ozone maximum on all three days is in keeping with the fact that a high pressure system was stationed over the eastern United States on these three days.

Figure 16 shows that on 27 August Site 1 experienced NO levels of the order of 15 ppb from 0600 to 0800. This indicates the arrival of air loaded with emissions from the morning traffic. However, the NO disappears quickly, being undetectable by 1000. On 28 August (cf. Figure 17) ozone levels remain high well into the evening and into the morning of 29 August, which was the same phenomenon observed during 4-5 August (Figures 14 and 15). Ozone decays rapidly from 0100 to 0400 on 29 August, building up again after 0600. On all three days, ozone concentration always exceeded 80 ppb between 1100 and 2100, indicating a persistent pollution condition; such was not the case in the episode of 3-5 August.

Trajectories arriving at Site 1 during 27-29 August are displayed in Figures 23-25. The pattern is remarkably similar to that seen earlier in Figures 20-22. Thus, high ozone levels occurring in the late afternoon and early evening are associated with southwesterly flows into the site. Moreover, the lack of ozone carryover into the early morning of 27 August corresponds to trajectories originating in southern Canada in regions where emissions may be lower, and to less severe stagnation conditions such as prevailed on this day. However, on 28 and 29 August trajectories originate in the southeastern United States and Figures 17 and 18 show evidence of overnight ozone carryover from the 28th into the 29th. As was seen earlier during the events of 4-5 August, the carryover ozone is quickly depleted between midnight and 0400, followed by a rapid ozone buildup that peaks at 1300. As previously suggested, this could indicate fumigation of transported ozone "stored" aloft in a thermally stratified atmosphere.

The high-ozone event on 1 September (Figure 19) shows a very late ozone buildup that begins at 1200 and peaks at 1700. One implication of this condition is that the $NO/NO_2/O_3$ null reaction is dominant until about 1000, resulting in no net ozone production; it also suggests that

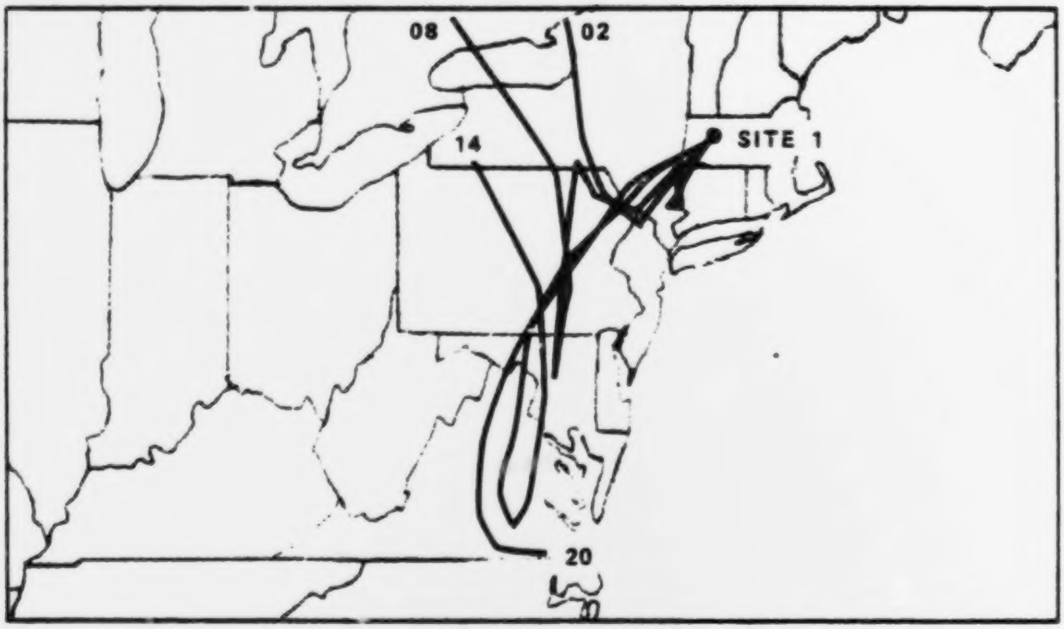

FIGURE 23 TRAJECTORIES ARRIVING AT SITE 1, MONTAGUE, MASSACHUSETTS, ON 27 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

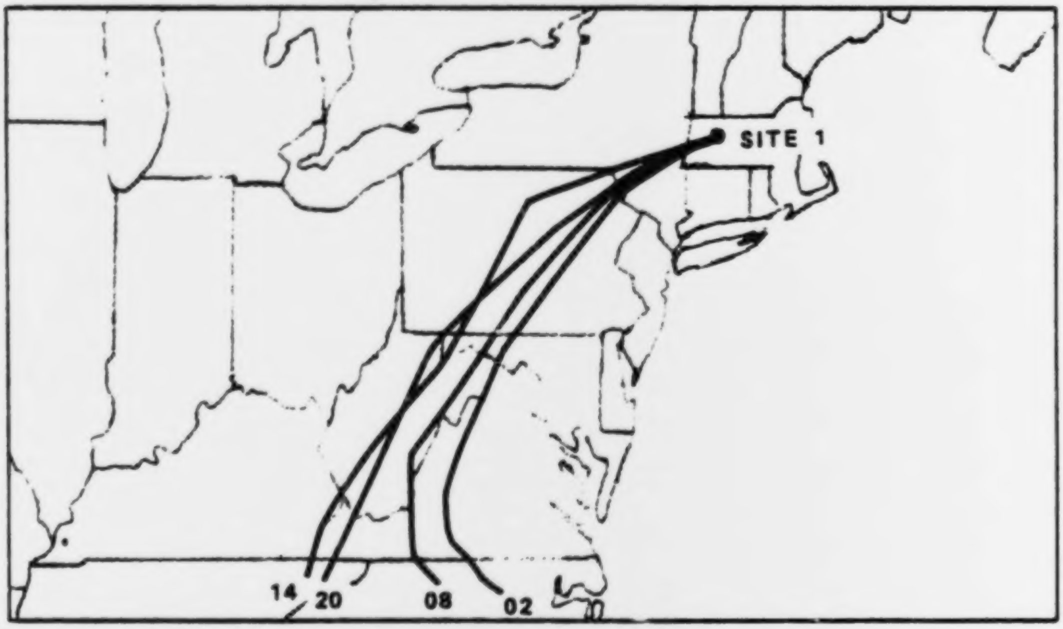

FIGURE 24 TRAJECTORIES ARRIVING AT SITE 1, MONTAGUE, MASSACHUSETTS, ON 28 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

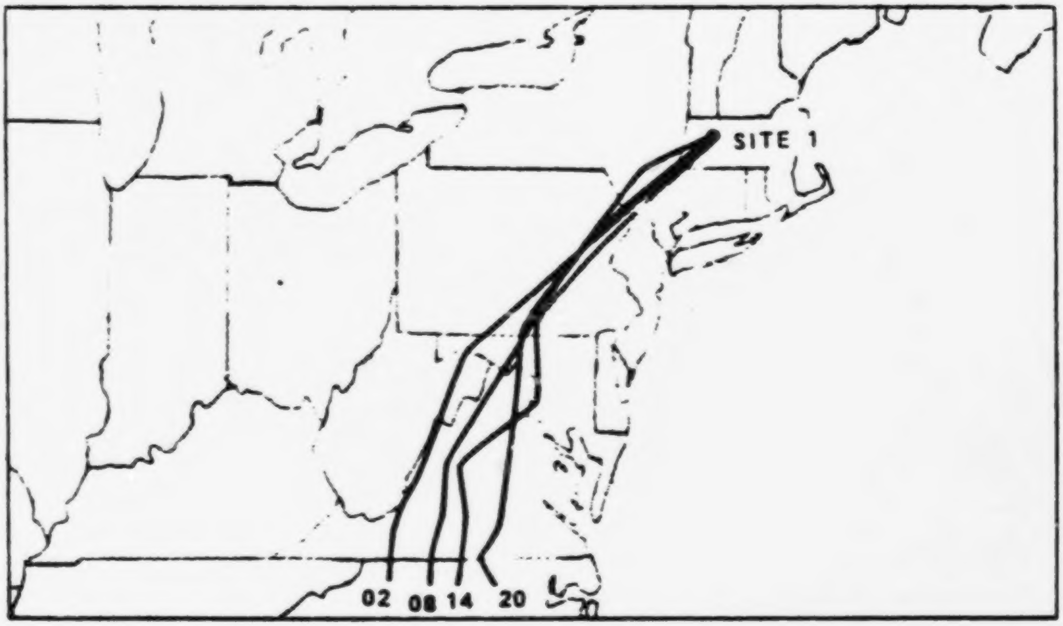

FIGURE 25 TRAJECTORIES ARRIVING AT SITE 1, MONTAGUE, MASSACHUSETTS, ON 29 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

the sky may have been overcast since ozone chemistry is so tightly coupled to sunlight intensity. The late peak is again indicative of ozone that has been transported to the site. It is interesting, however, that even after sunset the ozone tends to linger and actually increases late at night. This is consistent with the fact that the incoming air has very little NO to scavenge ozone.

Air masses arriving at Site 1 on 1 September are tracked in Figure 26, which shows the path of the air arriving at 0200 and 0800. (It was not possible to compute the other two trajectories because of data problems.) The trajectories are quite different from those seen earlier. This time the air takes a circuitous route to the site, implying that stagnation conditions and low wind speeds prevail. The latter may also be inferred from the node spacing in Figure 26. Part of the path of

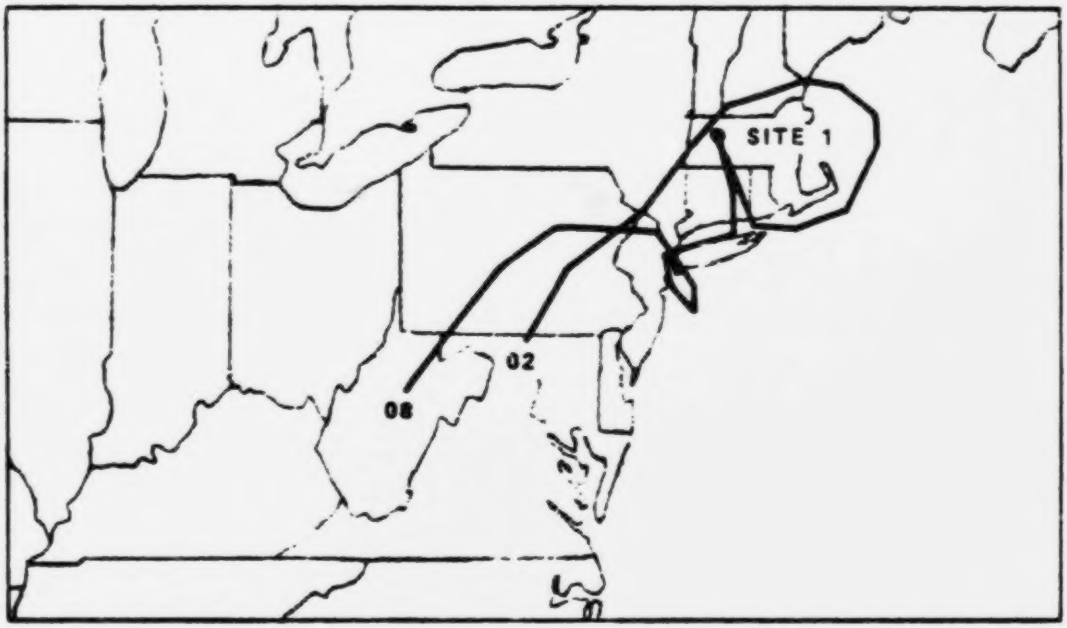

FIGURE 28 TRAJECTORIES ARRIVING AT SITE 1, MONTAGUE, MASSACHUSETTS, ON 1 SEPTEMBER 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

each trajectory is over the ocean, which may cause ozone levels to increase in the absence of NO sources (Graedel and Farrow, 1977). The convoluted path of the trajectories also suggests that the same air is being circulated about, which could account for the steady ozone level that prevails from midnight to 1100 (cf. Figure 19). If this meandering pattern were to continue throughout the day, it could also explain the relatively high nighttime ozone levels; however, we cannot confirm this.

In closing, it seems likely that most, if not all, the ozone peaks observed at Site 1 are attributable to transport. In addition to the lateness of some O_3 maxima, the evidence suggests the presence of a thermally stratified atmosphere, possibly leading to fumigation and an early afternoon peak the next day. The single-day episode of 1 September offers no evidence of thermal layering, but of a stagnant atmosphere where the air is being recirculated. This phenomenon is consistent with a transport explanation of the observations at Site 1.

While ozone transport seems to be the best explanation of these observations, this does not preclude the possibility of ozone enhancement by increased levels of NO_x. In all cases, NO levels are very low, but NO_2 shows slight fluctuations about 10 ppb, regardless of the ozone concentration. Is it possible, therefore, that increasing NO_x would lead to higher NO_2, and hence higher ozone? What would happen if the "steady" NO_2 concentration were 20 ppb instead of 10 ppb? We shall keep these questions in mind as we review the data for the other sites.

2. Case Study II: High-Ozone Events at Duncan Falls, Ohio (Site 4)

Ozone reached a maximum of 107 ppb at 1300 and 1400 on 2 September. This event was preceded by a maximum of 85 ppb on 1 September. A high-pressure system prevailed over the eastern United States, extending from North Carolina to Maine. The site appears to be located in what may be termed the back side of this high-pressure system. On 1 September a front was stationed west of Duncan Falls, with precipitation being reported in northern Illinois and western Michigan. This front moved closer to the site on 2 September, causing rain in northern Ohio. However, high-pressure conditions prevailed at the site on this day. The front passed over the site on the afternoon and evening of 2 September, and high-pressure conditions were reestablished by the morning of 3 September.

Figures 27 and 28 show the hourly variations in O_3, NO, and NO_2 at Site 4 on 1 and 2 September, respectively. Both days are characterized by ozone carryover during the night. Although nighttime ozone is low (about 30 ppb), the concentrations did not vanish, suggesting a relatively deep mixing layer and little or no chemical scavenging. NO and NO_2 were very low on these two days, with very little evidence of NO_2 carryover. Figure 27 displays an increase in O_3 between 1800 and 2000,

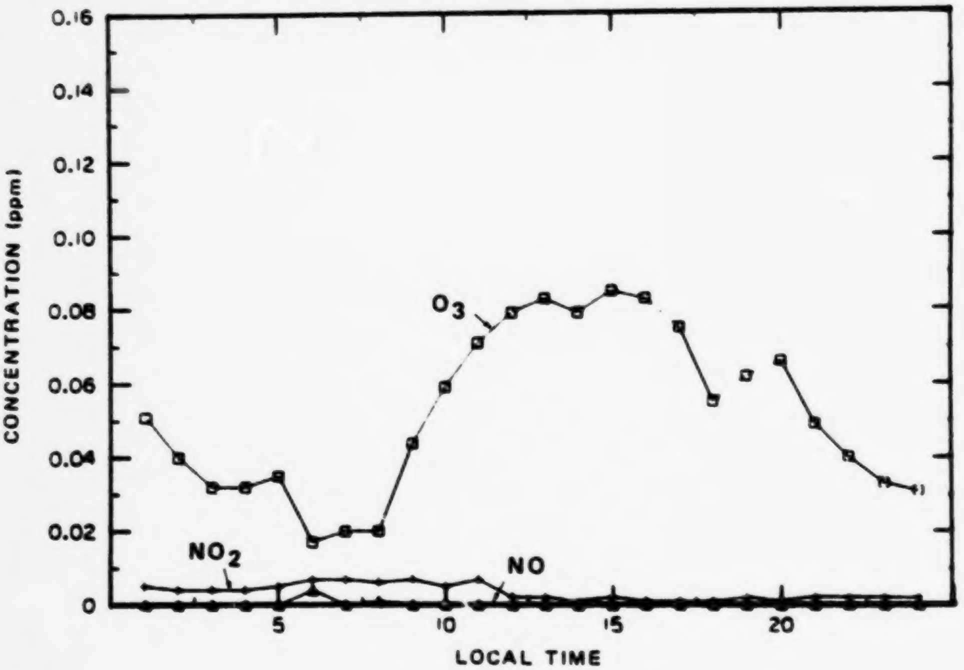

FIGURE 27 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 4 ON THURSDAY, 1 SEPTEMBER 1977

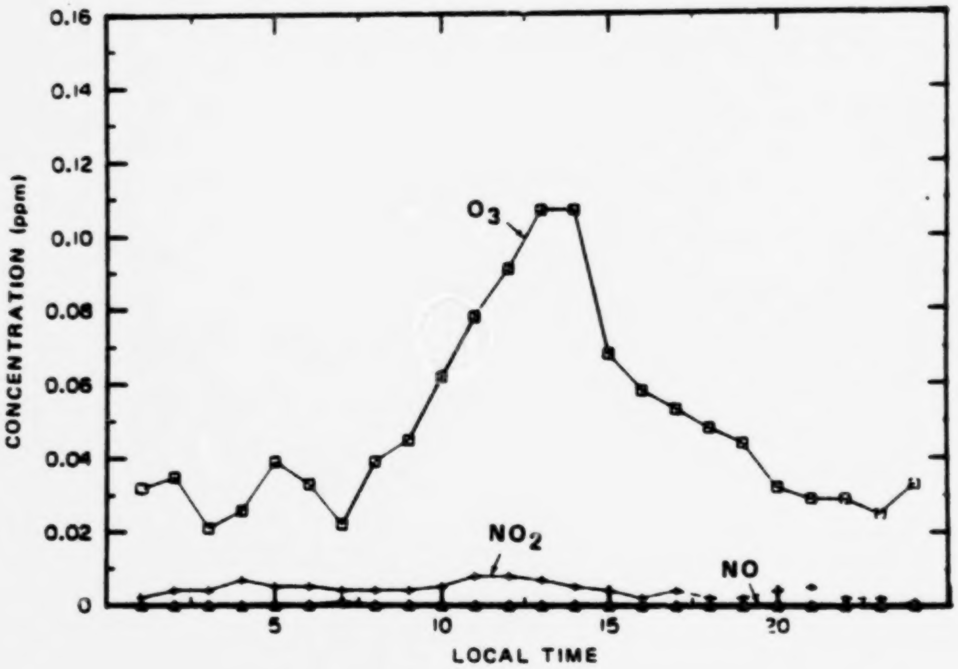

FIGURE 28 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 4 ON FRIDAY, 2 SEPTEMBER 1977

which is undoubtedly due to transport. On 2 September, the evidence also suggests transport effects, even though O_3 peaks early. Transport may be inferred, given the rural location and character of the site, but equally important is the fact that NO and NO_2 hardly change during the day, which indicates that the oxidation of NO to NO_2 is essentially complete in the incoming air mass.

Four trajectories arriving at Site 4 on 2 September are depicted in Figure 29. The air masses follow a semicircular path into the site, arriving from the southwest. Some of the trajectories (particularly those arriving between 0800 and 2000) probably passed over Cincinnati, which could account for the high ozone concentrations at Site 4.

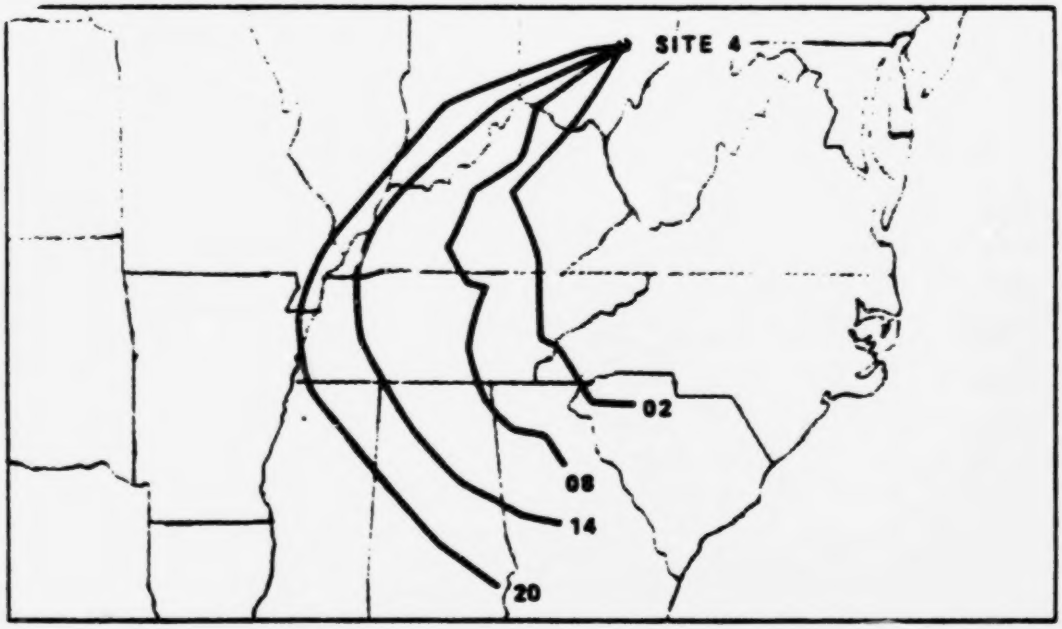

FIGURE 29 TRAJECTORIES ARRIVING AT SITE 4, DUNCAN FALLS, OHIO, ON 2 SEPTEMBER 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

An interesting feature of the data in Figures 27 and 28 is the very low level of NO_x that prevailed on these days. Once again we see substantial increases in O_3, but little change in NO_x. This would be expected to occur in a spent air mass. It is noteworthy that not only is there a low frequency of occurrence of high ozone levels, but also that the high concentration was below 120 ppb. Thus, while the "spent" air mass may be capable of producing ozone in excess of 80 ppb as suggested by smog chamber results (cf. Section II-H), it may be unable to yield levels above 120 ppb.

3. Case Study III: High-Ozone Days at Giles County, Tennessee (Site 6)

Ozone levels greater than 100 ppb were observed on 2 and 22 August and 23 September. A high-pressure system prevailed over the area on the first two days. However, a front was approaching on the 22nd. Mild weather was the norm on 23 September, a weak warm front being present over Indiana and Ohio.

Figures 30 to 32 show the daily variations of O_3 and NO_x on the three days of interest. We have shown NO_x instead of NO and NO_2 as in other figures because data for NO are missing. The trajectories that impact the site on these three days are depicted in Figures 33 through 35.

Transport influence is evident in Figures 30 and 32. On both occasions, the ozone peak occurs somewhat late, at 1900 and 1500 respectively, and its advent is sudden rather than gradual. Local photochemistry is apparent during the early morning buildup. These two days also have relatively high ozone levels late at night, reaching a value of about 50 ppb.

Trajectories arriving at Site 6 on 2 August and 23 September are displayed in Figures 33 and 35, respectively. The figures show that the early paths of both sets of trajectories have a similar north-south

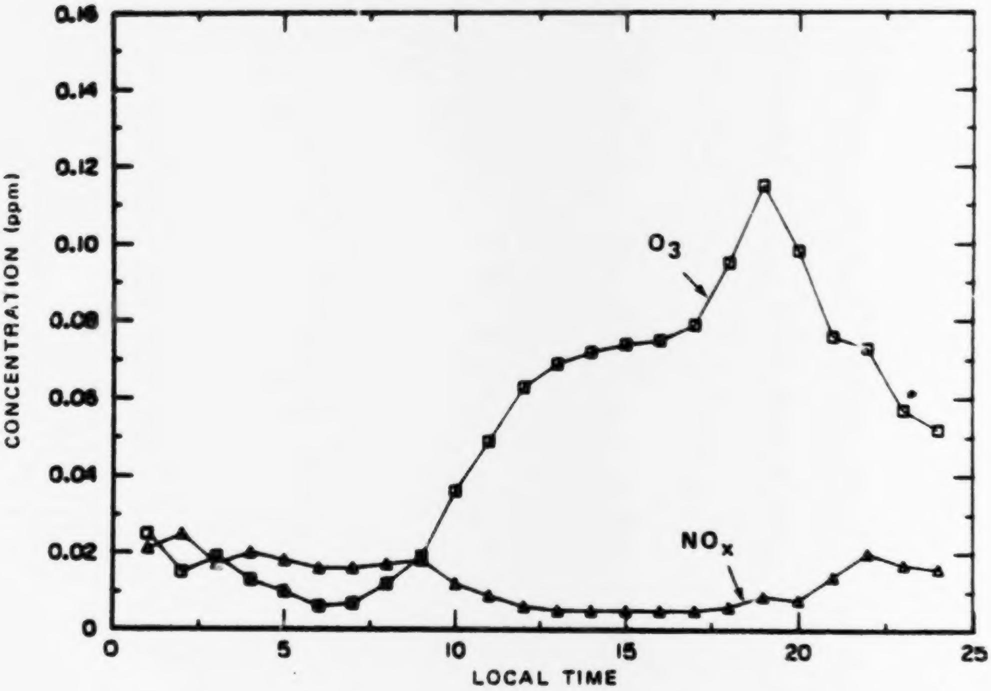

FIGURE 30 HOURLY CONCENTRATION VARIATIONS OF O_3 AND NO_x AT SITE 6 ON TUESDAY, 1 AUGUST 1977

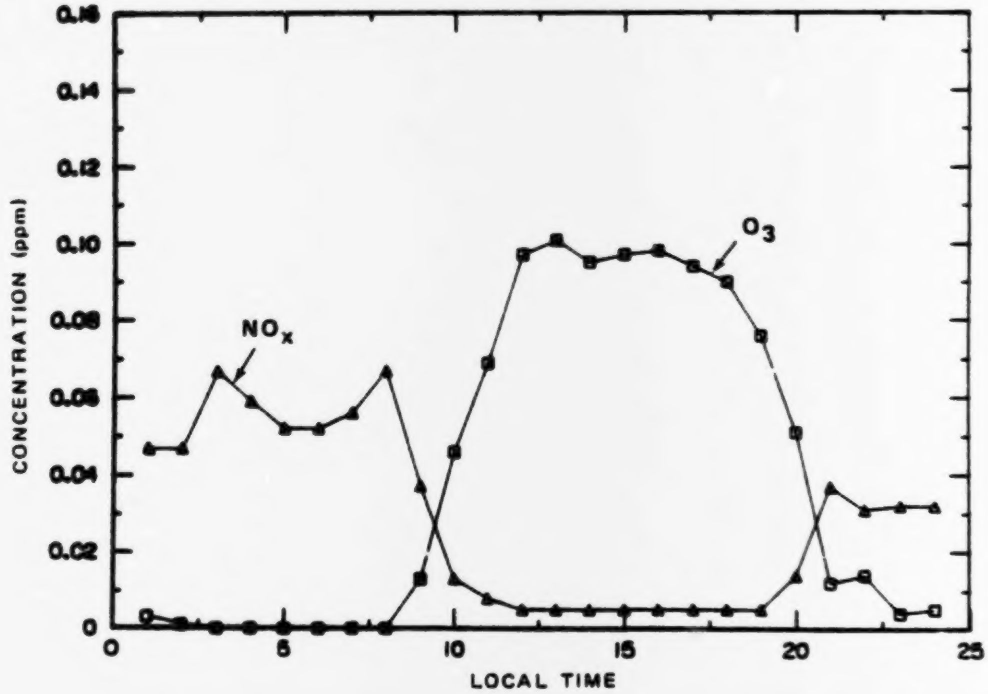

FIGURE 31 HOURLY CONCENTRATION VARIATIONS OF O_3 AND NO_x AT SITE 6 ON MONDAY, 22 AUGUST 1977

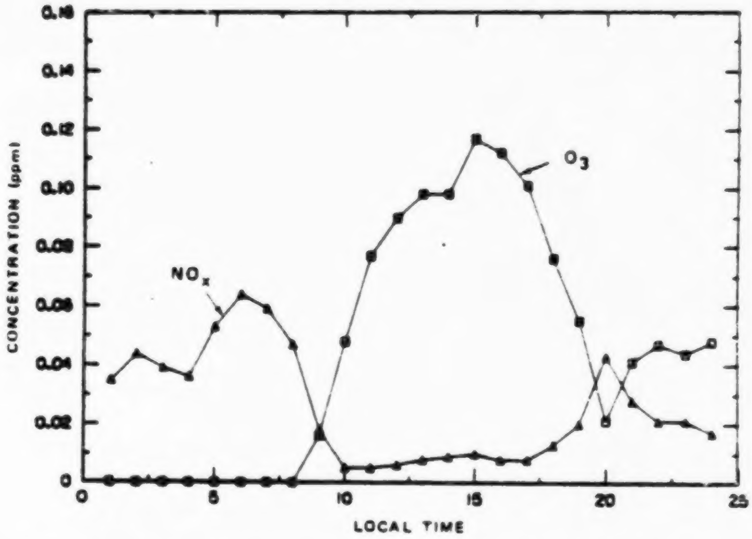

FIGURE 32 HOURLY CONCENTRATION VARIATIONS OF O_3 AND NO_x AT SITE 6 ON FRIDAY, 23 SEPTEMBER 1977

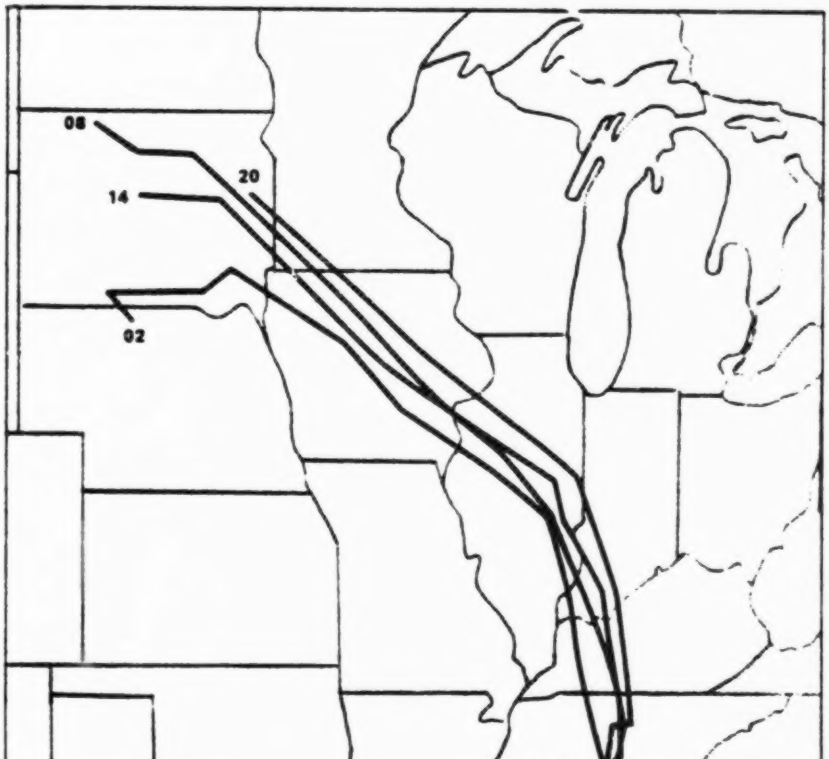

FIGURE 33 TRAJECTORIES ARRIVING AT SITE 6, GILES COUNTY, TENNESSEE, ON 2 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

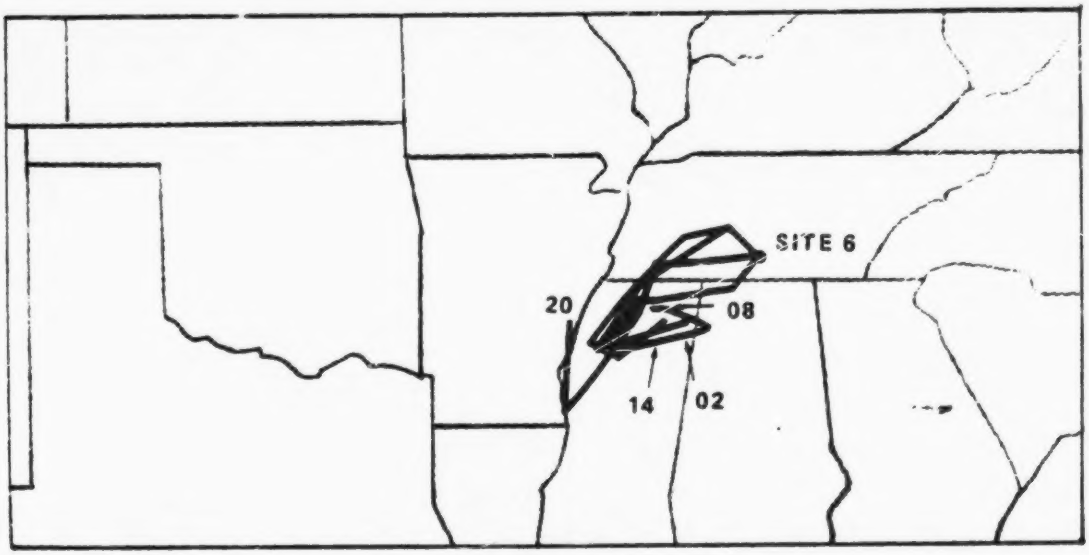

FIGURE 34 TRAJECTORIES ARRIVING AT SITE 6, GILES COUNTY, TENNESSEE, ON 22 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

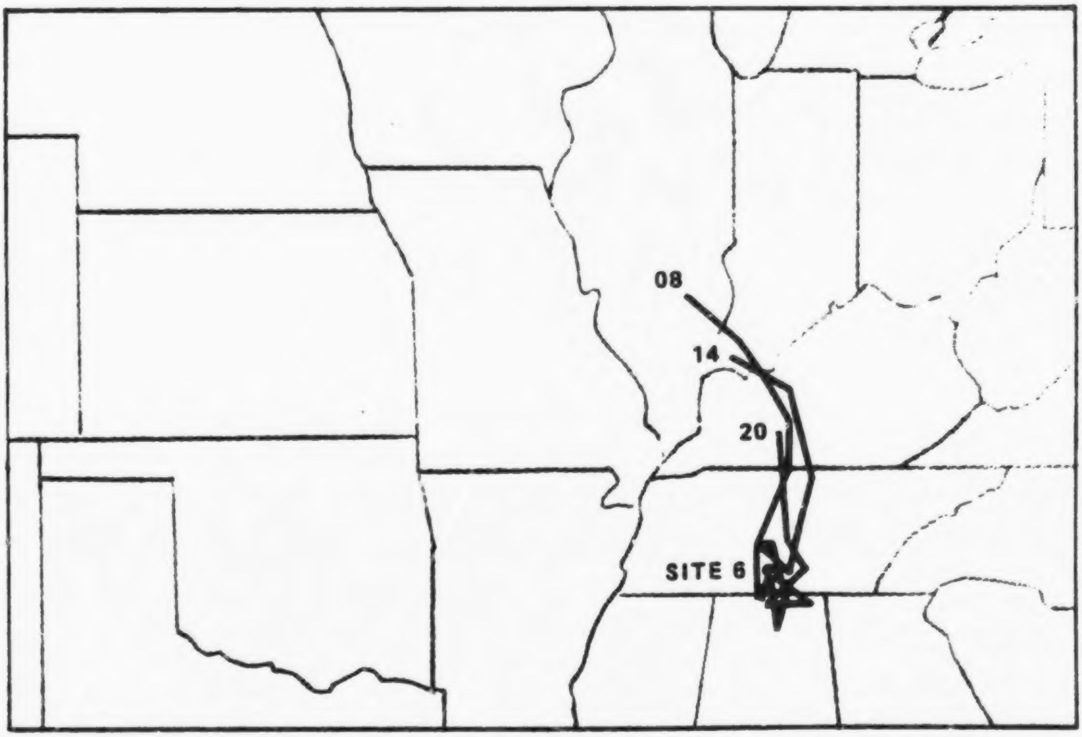

FIGURE 35 TRAJECTORIES ARRIVING AT SITE 6, GILES COUNTY, TENNESSEE, ON 23 SEPTEMBER 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

orientation. However, the trajectories for 2 August (Figure 33) are much longer than for 23 September (Figure 35), which indicates that meteorological conditions were less stagnant on 2 August than on 23 September. The convoluted path of the trajectories shown in Figure 35 is further indication of the presence of stagnant, low-wind conditions on 23 September.

Examination of the path of the trajectories suggests that the ozone peak that occurred at 2000 on 2 August (Figure 30) may be due to precursors that originated in the Nashville area, which is about 100 km northeast of Site 6. On 23 September, the ozone peak may be associated with an urban plume from Huntsville, Alabama, located about 40 km south of the site. It appears, therefore, that short-range transport is the primary influence at work on these two days.

The ozone maximum observed on 22 August is probably the result of local photochemistry. Figure 31 shows high NO_x in the morning and its rapid decay is accompanied by a buildup of ozone that peaks at 1300; NO_x remains low and essentially constant between 1300 and 2000, when its concentration increases. This day displays a sustained high ozone concentration that lasts from 1200 to 1800. In this interval, ozone concentrations do not differ much from the peak of 101 ppb. While the maximum is tied to local chemistry, the broadening of the ozone curve is most likely induced by transport.

Figure 34 shows that the trajectories on 22 August differ radically from those for 2 August and 23 September. On 22 August the wind flow is consistently from the west and southwest, and the trajectories are clustered over northern Mississippi and southwestern Tennessee. The convoluted track of the trajectories is symptomatic of low wind speeds and relatively stagnant conditions. In contrast to the other two days, 22 August shows no sudden increase in the ozone peak, but displays instead a broadening of the ozone maximum lasting several hours, and the peak ozone level is lower than on the other two days (cf. Figure 31). This discrepancy in pollutant history is undoubtedly a manifestation of the different wind flow patterns present on 22 August, but the origin of the transported ozone is unclear. No large urban areas appear to be on the path of the trajectories on this day, which may account for the lower ozone level and the absence of a sudden ozone increase.

Carryover ozone from the previous night is not significant on any of the three days. The same is true of NO_x on 2 August (cf. Figure 30). As the figures show, ozone builds up more rapidly when high levels of NO_x are present in the morning (cf. Figures 31 and 32) than when morning NO_x is low (cf. Figure 30). This implies that local photochemistry is most important during the early stages of ozone accumulation, but that its influence wanes as the day wears on. Consequently, the ozone maximum may or may not be due to local effects. At this site, it seems that local ozone production cannot result in very high ozone levels, but that transported ozone combined with local ozone can approach the 120-ppb ozone standard.

4. Case Study IV: High-Ozone Days at Research Triangle Park, North Carolina (Site 8)

Site 8 presents an interesting contrast to the monitoring stations previously considered: It is in a suburban location heavily impacted by traffic, and thus has the highest NO_x levels. Since the site is surrounded by three medium-sized cities, it is also a receptor for urban pollution.

Ozone exceeded 100 ppb on five days. One maximum occurred at 1500, and the others at 1600 and 1700. General weather conditions on the high-ozone days were variable. A high-pressure system was present on 9 and 26 August. High pressure also prevailed on 30 August, which preceded the high-ozone event of the 31st. A low-pressure center was stationed off the coast of Virginia on 10 September, low pressure and precipitation having prevailed in North Carolina for several days previously. On 23 September, a weak warm front was observed across the midwestern states, while stagnant to light wind conditions prevailed throughout the southeast. Thus, overall weather patterns were quite unlike those that accompanied the elevated ozone levels observed at Site 1. This partly accounts for the fact that four of the five cases are single-day episodes, the lone exception being the event of 9 August, and that ozone concentrations are not as high as were seen in Site 1.

Figures 36 and 37 show the pollutant variations on 8 and 9 August. The high ozone level of 9 August is characterized by considerable carryover from the previous day. The ozone maximum occurred late on both days, suggesting transport as the cause. NO and NO_2 are more abundant than at the other sites. In view of the abundance of precursors, it is probable that the early ozone peak is locally produced, rather than resulting from transport. The circulation patterns for 9 August are illustrated in Figure 38, the trajectories for 8 August being almost identical to these. As in other cases, the tracks are semicircular with a clockwise orientation typical of anticyclonic circulation. Because these trajectories do not appear to traverse any heavily polluted areas, it is likely that the transported pollutants originate in the Durham-Chapel Hill area, which is several miles west of Site 8.

Conditions on 26 August are depicted in Figure 39. As before, there is substantial carryover from the previous night. However NO_x levels are low during the day, which indicates the arrival of an aged mass of polluted air. As seen in Figure 40, the trajectories are again typical of anticylonic circulation, with the air passing over the heavily congested Washington D.C. area. Wind speeds near the site are relatively low, and the southeasterly direction points to Raleigh as the source of pollutants.

On 31 August (Figure 41) a typical NO traffic peak is evident in the morning. The NO decays rapidly, but with no attendant increase in NO_2; in fact, NO_2 decreases sightly in spite of the rapid disappearance of NO, thereby suggesting that, in addition to chemical reaction,

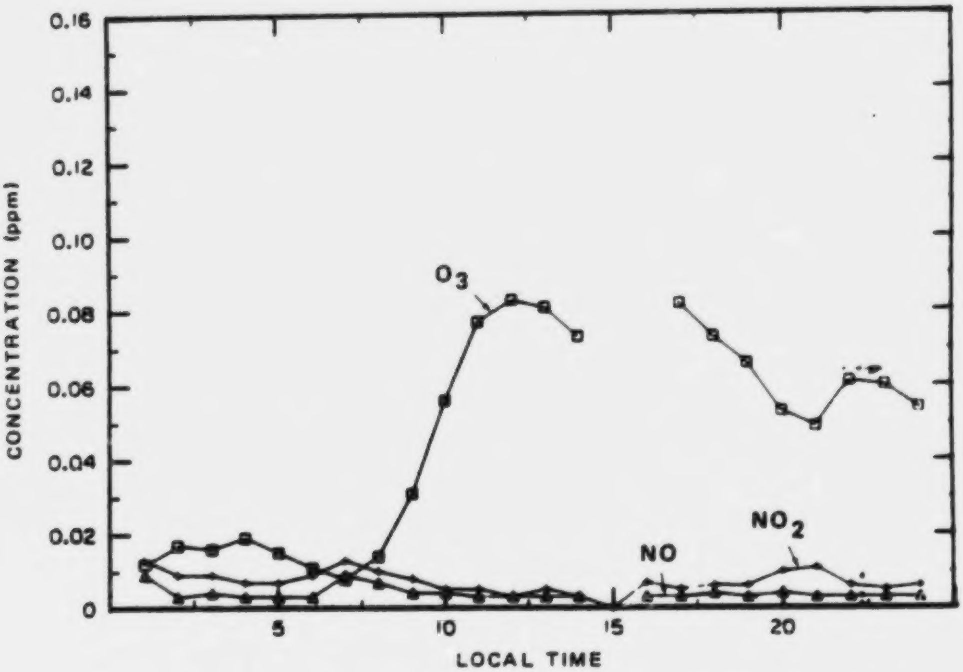

FIGURE 36 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 8 ON MONDAY, 8 AUGUST 1977

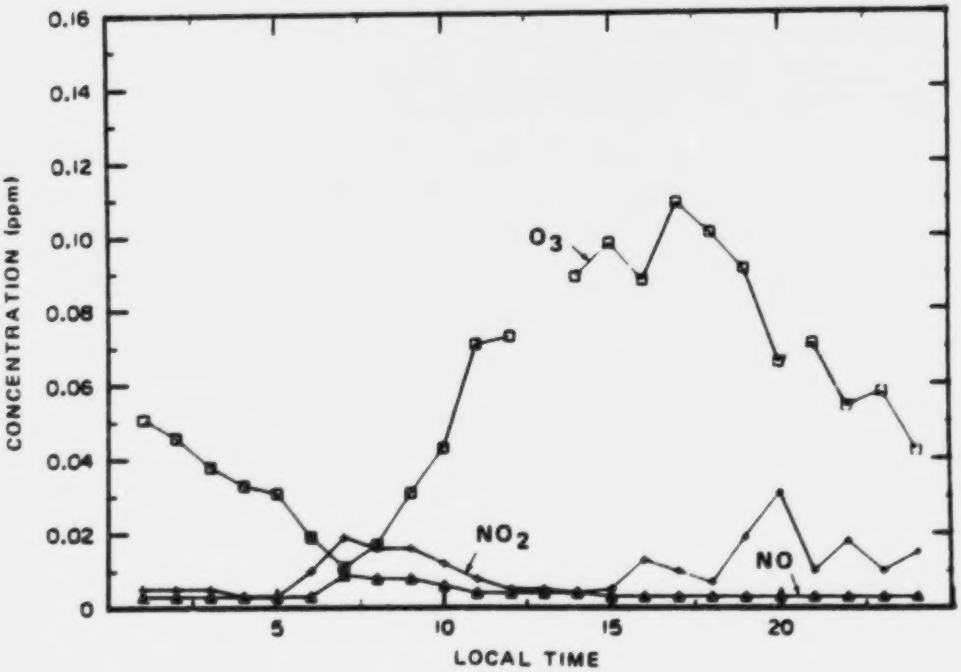

FIGURE 37 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 8 ON TUESDAY, 9 AUGUST 1977

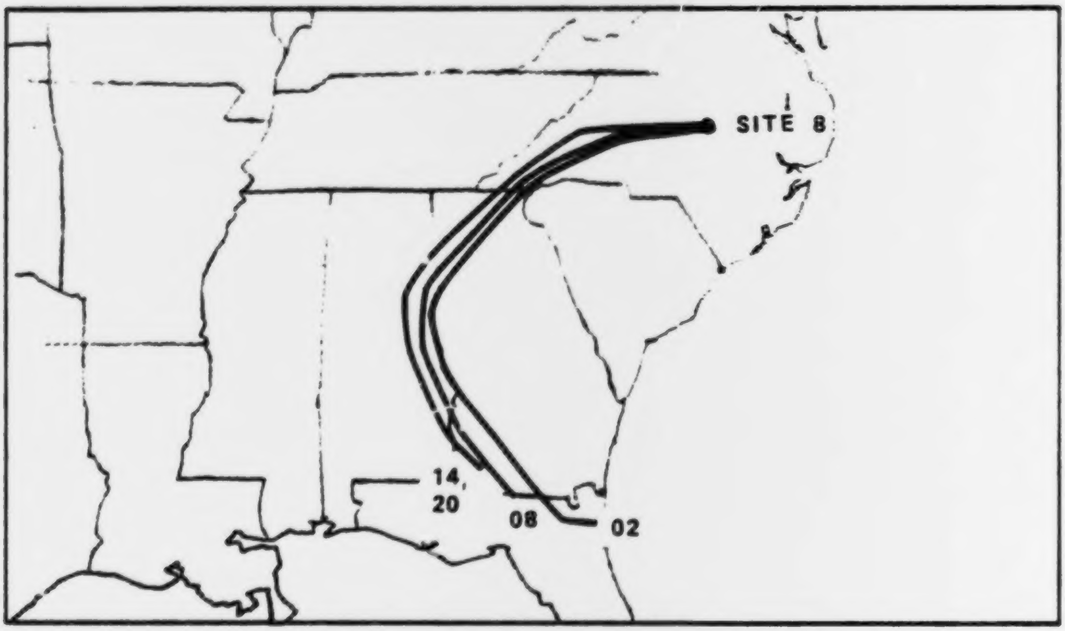

FIGURE 38 TRAJECTORIES ARRIVING AT SITE 8, RESEARCH TRIANGLE PARK, NORTH CAROLINA, ON 9 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

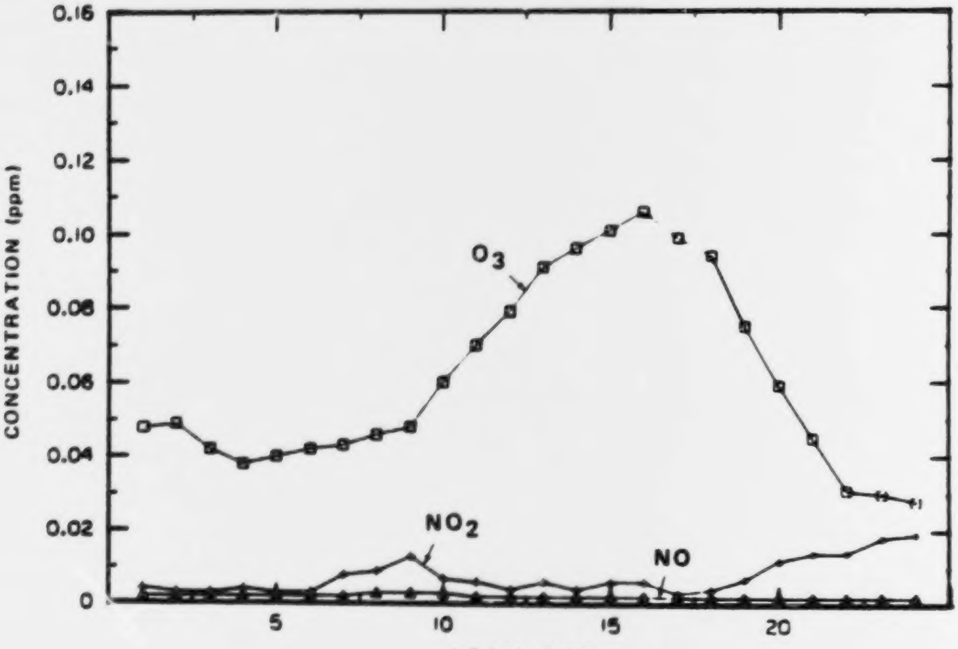

FIGURE 39 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 8 ON FRIDAY, 26 AUGUST 1977

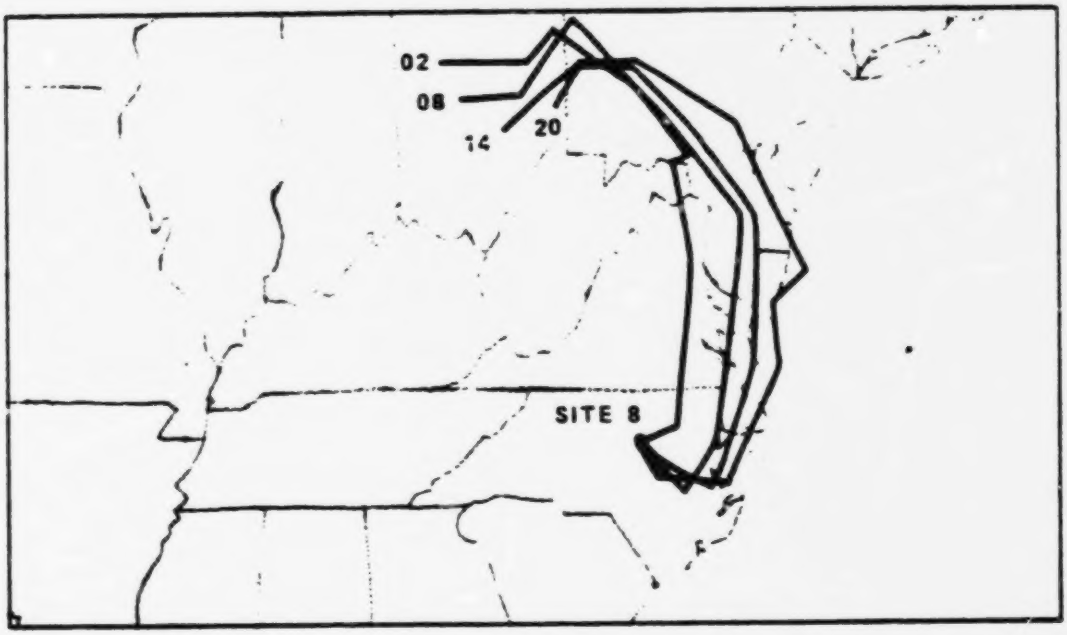

FIGURE 40 TRAJECTORIES ARRIVING AT SITE 8, RESEARCH TRIANGLE PARK, NORTH CAROLINA, ON 26 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

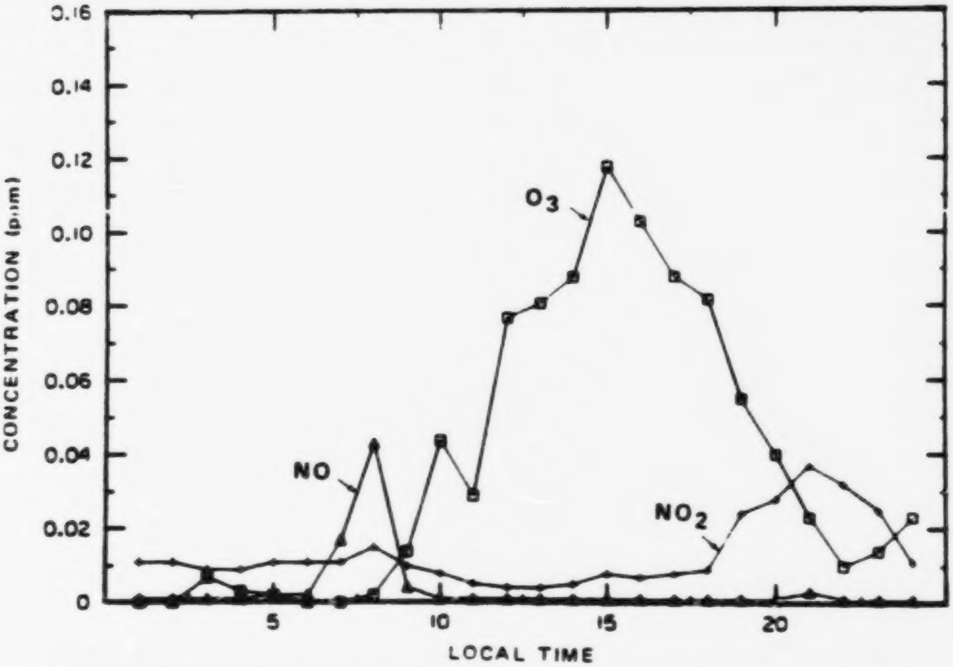

FIGURE 41 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 8 ON WEDNESDAY, 31 AUGUST 1977

dispersion is causing some of the NO and NO_2 decay. The jaggedness in the ozone curve may result from fluctuations in radiation intensity. The sudden appearance of the ozone peak and the relatively late time of its occurrence suggest that transport plays a significant role.

Trajectories arriving at Site 8 on 31 August are depicted in Figure 42. It is evident that between 0200 and 1400 prevailing winds are from the west. Hence, pollutants originating in the vicinity of Durham are probably responsible for the ozone peak that occurs at 1500. The wind has shifted to an easterly direction by 2000, coinciding with an increase in NO_2 that begins at 1900. Since Raleigh is located east of Site 8, it is likely that the increased NO_2 is associated with an urban plume from this city.

Figure 43 illustrates the pollutant history of 10 September. Recall that weather conditions on this day included a low-pressure center off Virginia. Cyclonic conditions are in evidence in Figure 44, which shows air trajectories for this day. Clearly, the trajectories are oriented counterclockwise and meander considerably. The early morning air is probably clean, having come off the Atlantic. The air arriving at 1400 appears to have passed over the Durham area. The indications are that the morning ozone buildup is from local causes, and that the high concentrations between 1300 and 1600 are sustained by transport from nearby communities. The lack of hourly fluctuations in NO is probably explained by the lower level of traffic that would prevail on a Saturday.

The pollutant histories on 23 September, displayed in Figure 45, show that very high NO and NO_2 levels were present. The large early NO_x concentration suggests a low inversion that allowed them to accumulate. In contrast to the other days at Site 8, there is considerably carryover of NO and NO_2 from the previous day. Since NO is so high, ozone essentially vanishes. NO peaks at 0800 and quickly disappears thereafter, allowing O_3 to accumulate. Ozone continues to build up until 1700, when

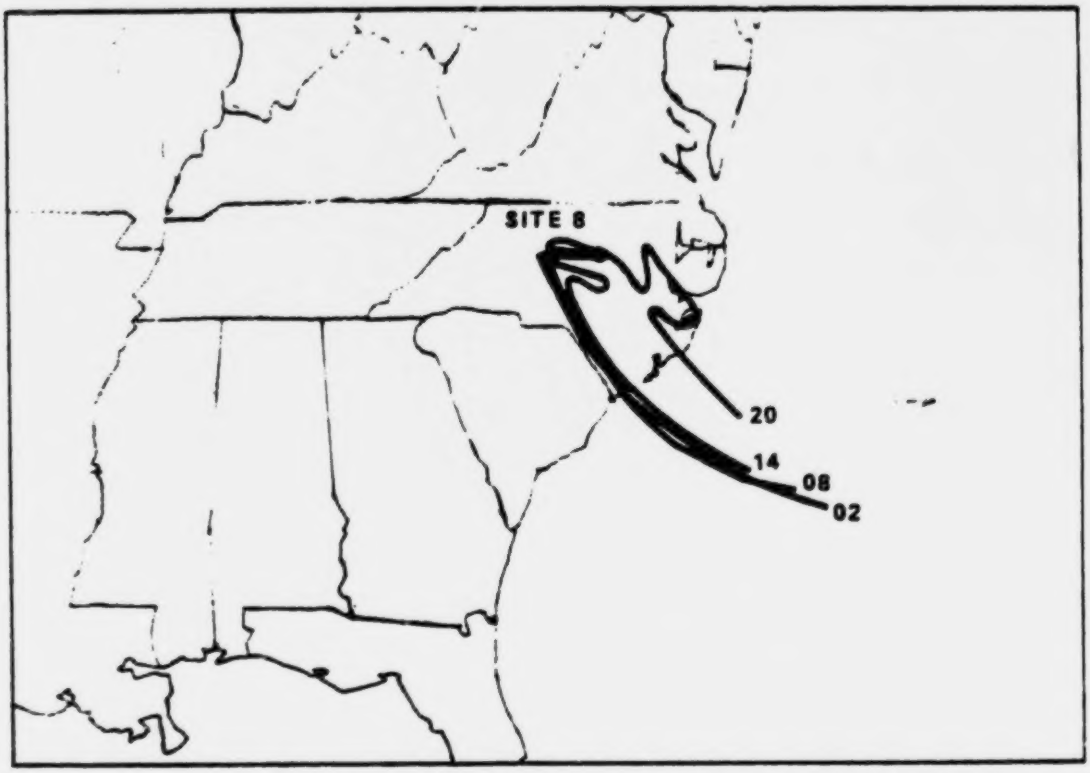

FIGURE 42 TRAJECTORIES ARRIVING AT SITE 8, RESEARCH TRIANGLE PARK, NORTH CAROLINA, ON 31 AUGUST 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

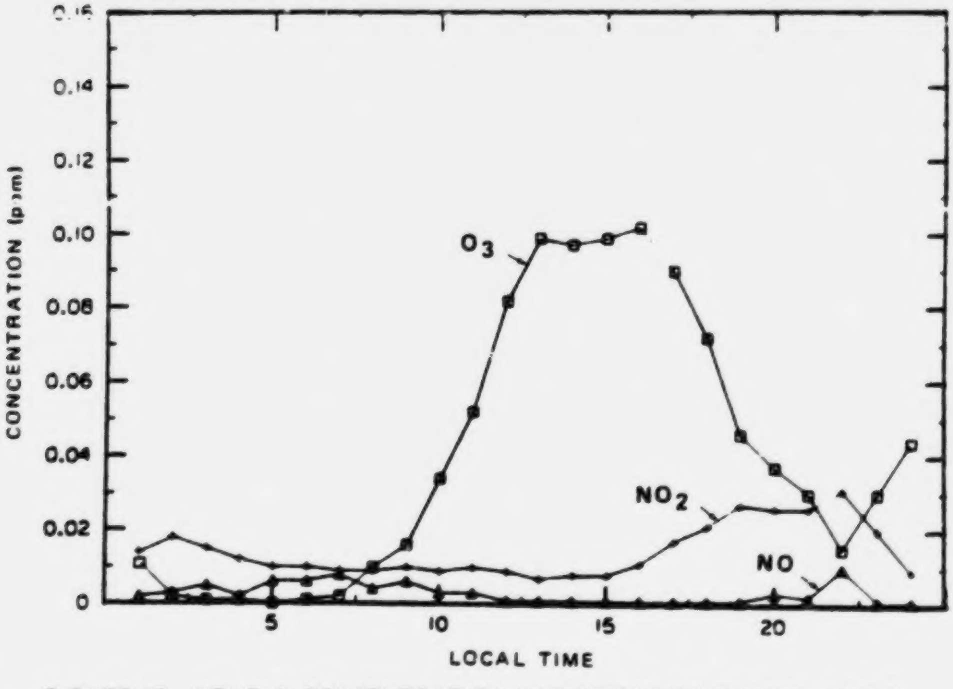

FIGURE 43 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 8 ON SATURDAY, 10 SEPTEMBER 1977

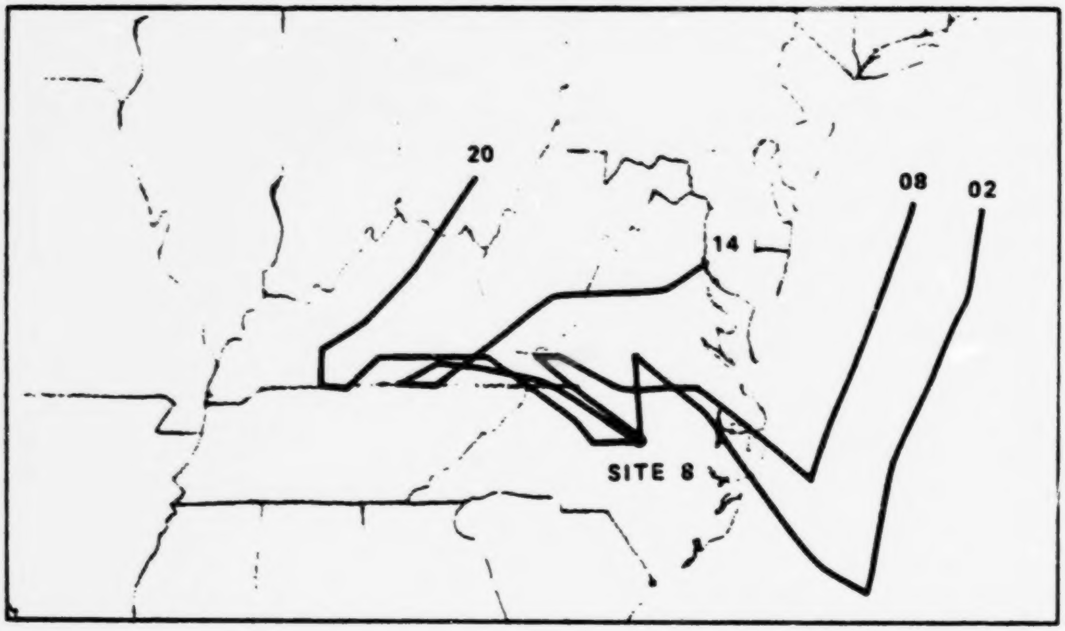

FIGURE 44 TRAJECTORIES ARRIVING AT SITE 8, RESEARCH TRIANGLE PARK, NORTH CAROLINA, ON 10 SEPTEMBER 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

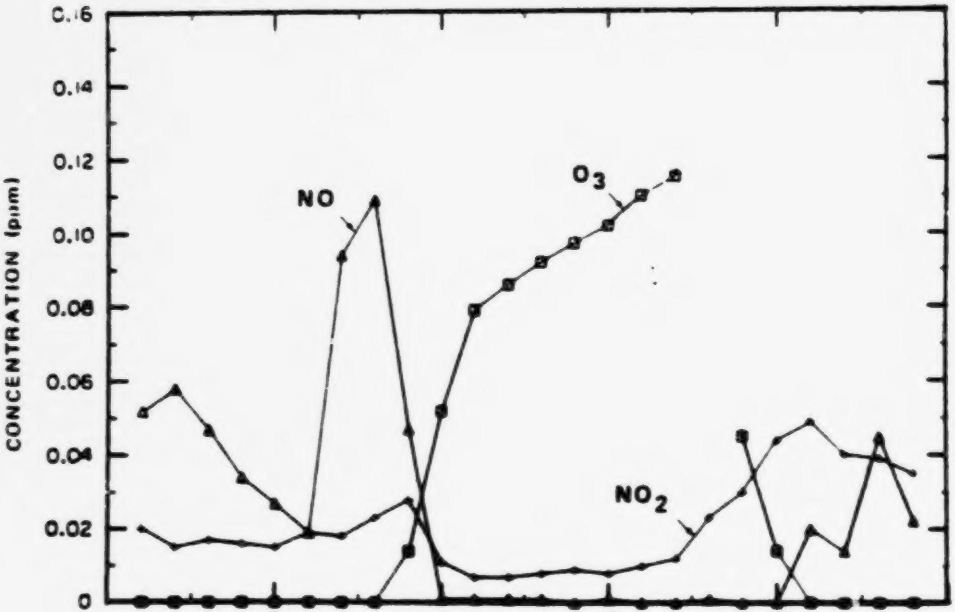

FIGURE 45 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 8 ON FRIDAY, 23 SEPTEMBER 1977

there is a break in the data. Meanwhile, NO_2 stays at about 10 ppb until 1700, when it begins to increase.

Figure 46 displays the trajectories arriving at Site 8 on 23 September. Between 0200 and 1400 the air travels over the Washington, D.C. area on its way to Site 8, which suggests that pollutants from this region impact Site 8. A long- or medium-range ozone transport hypothesis is consistent with the appearance of the ozone peak at 1700 (cf. Figure 45). Thus, while local factors are no doubt responsible for the ozone buildup between 0800 and 1100, transport effects are the likely causes of the higher ozone levels that occur after 1100.

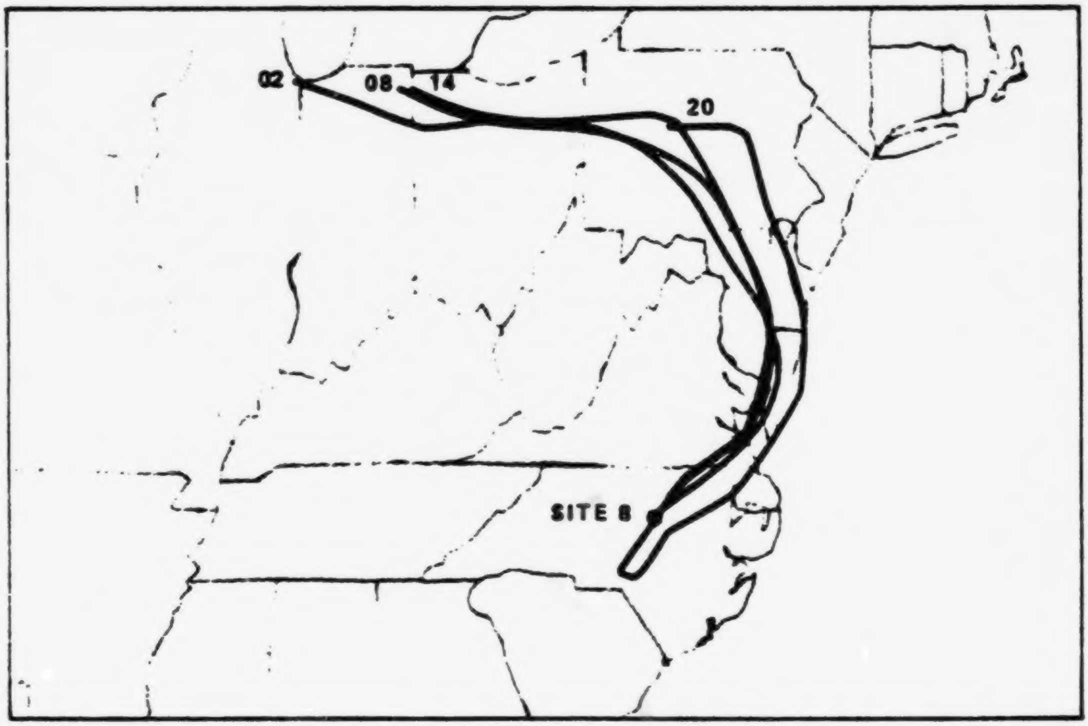

FIGURE 46 TRAJECTORIES ARRIVING AT SITE 8, RESEARCH TRIANGLE PARK, NORTH CAROLINA, ON 23 SEPTEMBER 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

The investigation of ozone maxima at Site 8 reveals a mixture of local and transport effects. This is not unexpected for a suburban location where automobile emissions can be a dominant factor. However, if we could separate local and transport impacts, we would hypothesize that the higher ozone levels, which generally occur late in the day, are associated with transport from both Durham and Raleigh, depending on wind direction. The lower values are more likely to be of local origin.

5. Case Study V: High Ozone at Lewisburg, West Virginia (Site 9)

A maximum hourly ozone level of 106 ppb was observed at Site 9 on 22 October. Figure 47 illustrates pollution conditions on this day: some ozone carryover from the previous night, an O_3 buildup that begins late, at 0900, and very little NO_x. Ozone peaks late, at 1600, remains high for the rest of the day, then decays slowly until midnight, when its concentration reaches 60 ppb.

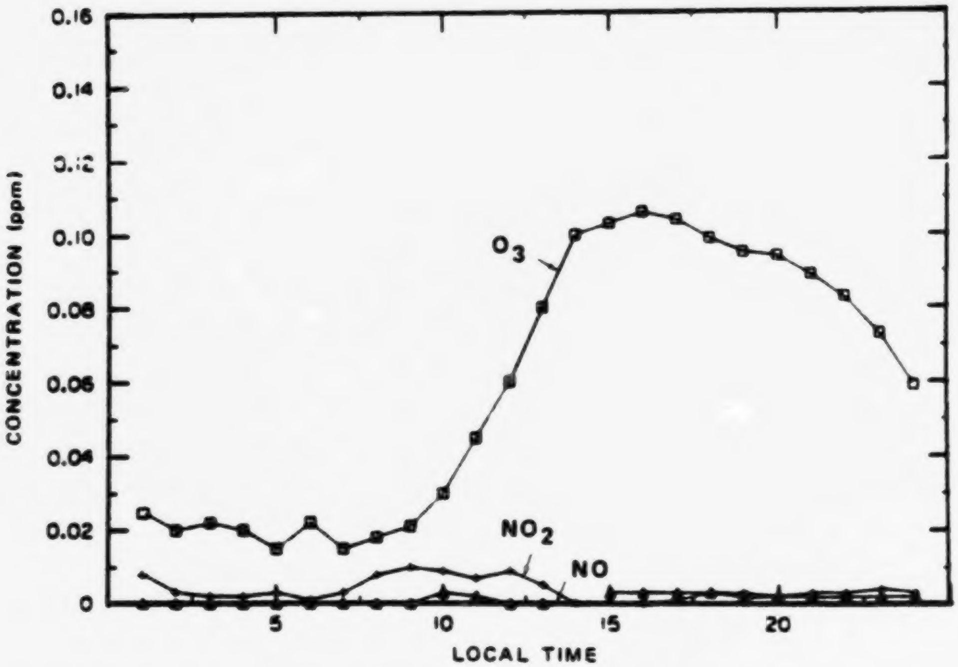

FIGURE 47 HOURLY CONCENTRATION VARIATIONS OF NO, NO_2, AND O_3 AT SITE 9 ON SATURDAY, 22 OCTOBER 1977

Meteorological patterns on 22 October, a Saturday, include a high pressure system off the coast of North Carolina, the system covering most of the eastern United States and reaching well beyond West Virginia. However, a front approximately aligned across the United States from New Mexico to New York is moving toward the southeast, passing over Site 9 on the morning of 23 October, bringing behind it another high-pressure system. The presence of a high-pressure system on the 22nd is manifested in the trajectories shown in Figure 48. While the trajectories follow a slight anticyclonic pattern, this is weakened by the front. The air masses arrive at the site from directions ranging between west and southwest. It is unlikely that the air masses passed over any major urban areas within 12 hours before arriving at Site 9.

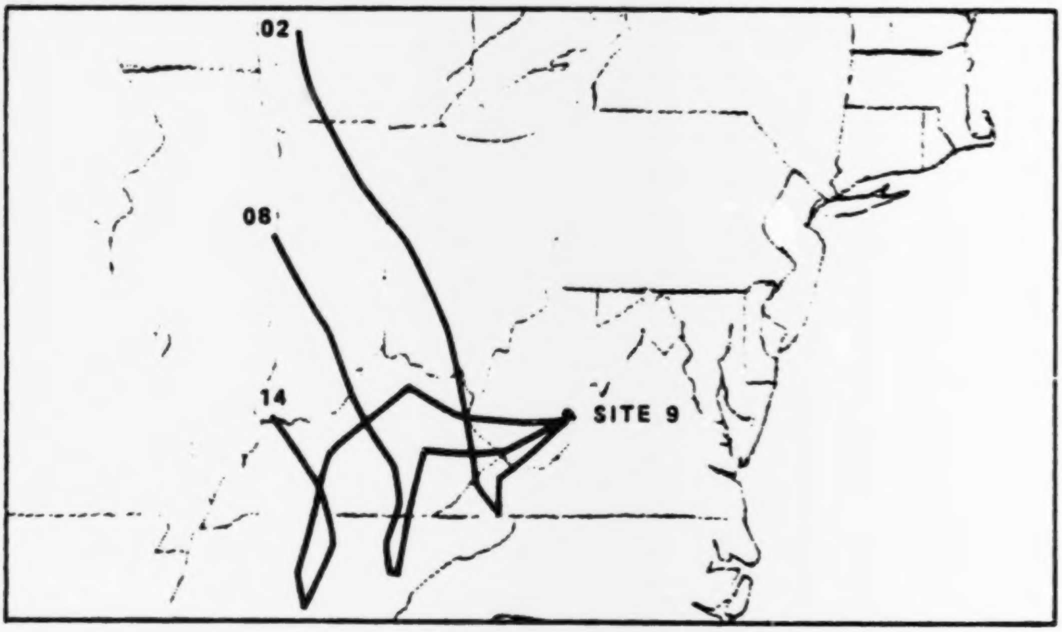

FIGURE 48 TRAJECTORIES ARRIVING AT SITE 9, LEWISBURG, WEST VIRGINIA, ON 22 OCTOBER 1977

The number shown at one extreme of a trajectory is the local time of arrival at the site.

The pollutant histories shown in Figure 47 imply that the high ozone observed at Site 9 is due to transport. However, the origin of the air is unclear from the trajectory analysis. Once again, NO_x levels are very low, yet O_3 remains at about the same level for several hours. Thus, ozone is neither made nor destroyed; NO_x appears to be superfluous in this case.

D. Conclusions

Ozone levels greater than 100 ppb were observed on a total of sixteen days at five sites, which included all four rural sites (Sites 1, 4, 6, and 9) and one suburban location (Site 8). Five of the high-ozone days occurred at Site 8, six at Site 1, three at Site 6, and one each at Sites 4 and 9. It is significant that all the locations that are least susceptible to localized sources exhibited high ozone levels, whereas four of the five suburban locales did not. This phenomenon is typically observed in urban regions, where ozone levels are often lower than in areas with a lower source density.

Influence of transport was evident on all the occassions when ozone was greater than 100 ppb. Transport was the most likely cause of the high ozone on eleven of the sixteen days, and both local chemistry and transport were present on the other five days. Local effects are indicated on 27 August at Site 1 (cf. Figure 16), 22 August and 23 September at Site 6 (cf. Figures 31 and 32), and 31 August and 23 September at Site 8 (cf. Figures 41 and 45). Figure 41 shows that on 31 August the local chemistry at Site 8 is dominated by traffic-related precursors, evidenced by the NO peak that occurs at 0800. Figure 45 also exhibits a traffic-induced NO peak at 0800, but there is evidence of a substantial amount of precursors present before 0500. In the five cases where local chemistry is important, local effects lead to a rapid ozone buildup, which usually reaches levels below 100 ppb. After ozone reaches a maximum, transport effects act to lengthen the time when ozone levels remain high. Transported ozone also combines with the local product to exceed 100 ppb.

An interesting aspect of the high-ozone days at the SURE sites is that the variations in the concentrations of NO_x are remarkably small compared to those of ozone. Moreover, the absolute levels of NO_x are quite low during the day. At Site 1, for example, NO is less than 1 ppb most of the time, and NO_2 fluctuates between 5 and 15 ppb, while ozone variations span a range of 100 ppb or more. The same is true at Sites 4 and 9, and is often the case at Sites 6 and 8. Using the available data, it is difficult to attribute this phenomenon to a particular factor. Thus, it is apparent that ozone fluctuations are heavily influenced by the sunlight cycle, and that there is sufficient NO_x to produce the observed ozone. But we have no data on the $NMHC/NO_x$ ratio at these sites, and the NO levels are so low that the NO_2/NO ratio can fluctuate over a wide range owing to uncertainty in the NO measurements. Thus, basic data are lacking to characterize the relationship between NO_x and O_3 at these sites. Recommendations to remedy this situation are provided in Section VII of this report.

V ANALYSIS OF JETMORE, KANSAS, DATA

A. Introduction

SRI recently conducted a study for the Coordinating Research Council (CRC), the main objective of which was to measure concentrations of natural O_3 in the free troposphere and determine mechanisms by which stratospheric O_3 was transported into the troposphere. An aircraft was equipped with O_3, NO/NO_x, and meteorological instrumentation to make these measurements to an altitude of 7 km. To complement aircraft data, a ground station was set up in a rural location.

The ground station operated between 4 April and 18 May 1978 at Jetmore, about 20 miles north of Dodge City (38°N, 100°W), Kansas. The site was specifically chosen because it is a clean site removed from sources of contamination. The ground station continuously measured CH_4, CO, THC, NO, NO_2, O_3, and various meteorological parameters. Other species of interest were measured in a batch mode. Table 19 provides a list of chemical and meteorological parameters measured at the ground station. The air quality instrumentation used is listed in Table 20. In the following sections we discuss the characteristics of the air quality data.

Because of the high quality of the measurements and the rural nature of the monitoring site, the data are useful for the purposes of this study.

B. Ground Station Data

Before proceeding with the data analysis, it is useful to note that the Jetmore site was a clean site only infrequently and marginally affected by urban transport. An indication of the cleanliness of the air can be obtained from Table 21, which lists the average concentrations of several chemicals measured during the study. The average methane and CO concentration of 1650 and 175 ppb, respectively, are

Table 19

CHEMICAL AND METEOROLOGICAL PARAMETERS MEASURED AT JETMORE, KANSAS

Chemical Parameters	Meteorological Parameters
O_3	Temperature at two levels
NO, NO_2	Wind speed at two levels
C_1 to C_5 hydrocarbons: CH_4, C_2H_6, C_3H_8, C_3H_6 i-C_4H_{10}, n-C_4H_{10}, i-C_5H_{12} and n-C_5H_{12}	Wind direction at two levels
	Solar flux
	Relative humidity
Fluorocarbon 12	
CO	
PAN	
Beryllium-7 (^{7}Be)	

Table 20

SRI MOBILE RESEARCH LABORATORY INSTRUMENTATION

Parameter	Instrument
Ozone	Bendix 8002 Chemiluminescent analyzer
NO/NO_x	Monitor Labs Model 8440E (specially modified for greater sensitivity)
C_1-C_5 Hydrocarbons	Perkin Elmer 3920 GC with FID
Fluorocarbon 12	Perkin Elmer 3920 GC with ECD
CO-CH_4-THC	Bendix 6800
PAN	Dual ECD Coulometer
Beryllium-7 (^{7}Be)	GIHA high-volume sampler Ge (Li) detector

Table 21

AVERAGE CONCENTRATIONS
OF SELECTED SPECIES
AT JETMORE, KANSAS

Compound	Concentration
CH_4	1650 ppb
CO	175 ppb
C_2H_6	20.7 ppbC
C_3H_8	9.9 ppbC
i-C_4H_{10}	3.2 ppbC
n-C_4H_{10}	8.4 ppbC
i-C_5H_{12}	3.2 ppbC
n-C_5H_{12}	3.6 ppbC
C_2H_4	0.8 ppbC
C_3H_6	0.8 ppbC
Fluorocarbon 12	240 ppt
PAN	≈0.4 ppb
NO_2	4 ppb
NO	1 ppb

close to their expected background levels. The average concentration of 20.7 ppbC for C_2H_6 was higher than expected. Propane, butanes, and pentanes were all present at concentrations of a few ppbC, as shown in Table 21. The NMHC have a concentration of about 50 ppbC. Table 21 makes it clear that alkenes are present at extremely low concentrations.

Figure 49 shows that CH_4 has a steady mean diurnal concentration. The HC levels are typical of clean sites at ground level. It is important to note that all alkenes added up to only 1.6 ppbC. On the other hand the alkanes (C_2 and above) approached 50 ppbC. Even if one

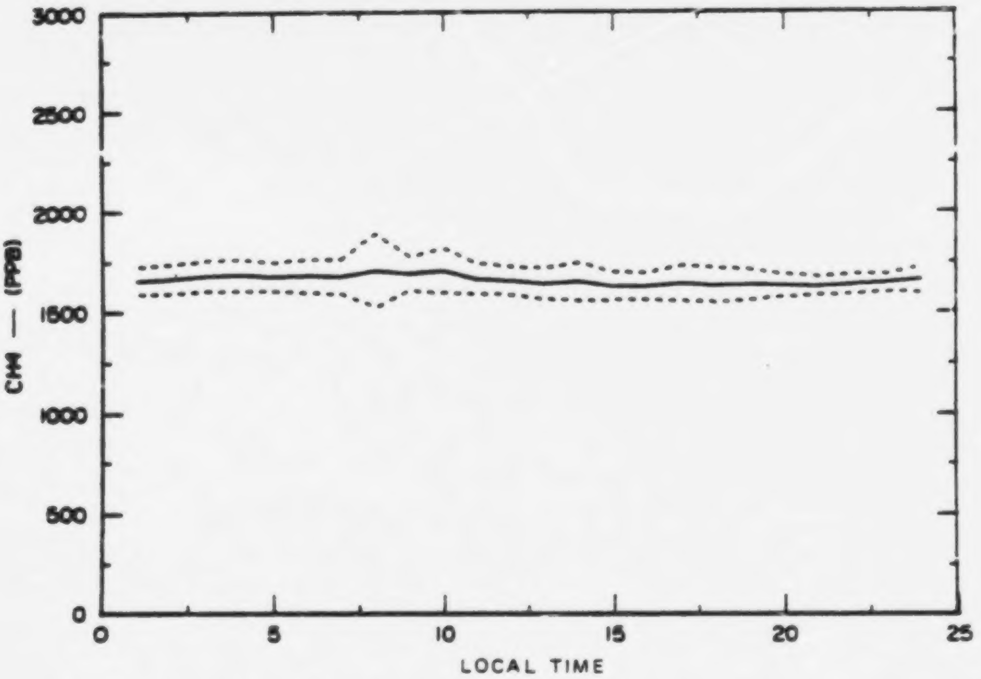

FIGURE 49 MEAN DIURNAL VARIATION IN CH_4 AT JETMORE, KANSAS, 3 APRIL-20 MAY 1978

excluded ethane as being relatively unreactive, the concentration of C_3 to C_5 alkanes was roughly 20 times that of the alkenes. The concentrations of CH_4 and C_2H_6 are higher than what is typically encountered in rural or remote locations. This, however, is not entirely surprising because of the large number of gas fields in the region; such fields are known to be significant sources of CH_4 and C_2H_6. Furthermore, while we only measured light hydrocarbons, it appears that there were no other organic compounds of higher molecular weight present here. The total HC measurement was nearly identical to the CH_4 level. Attempts made by Washington State University to measure aromatics at this site found these to be virtually nonexistent.

Figure 50 shows the mean diurnal variations of carbon monoxide (CO) at Jetmore. CO is not released from gas fields and is therefore a good indicator of urban transport. The average CO concentrations of

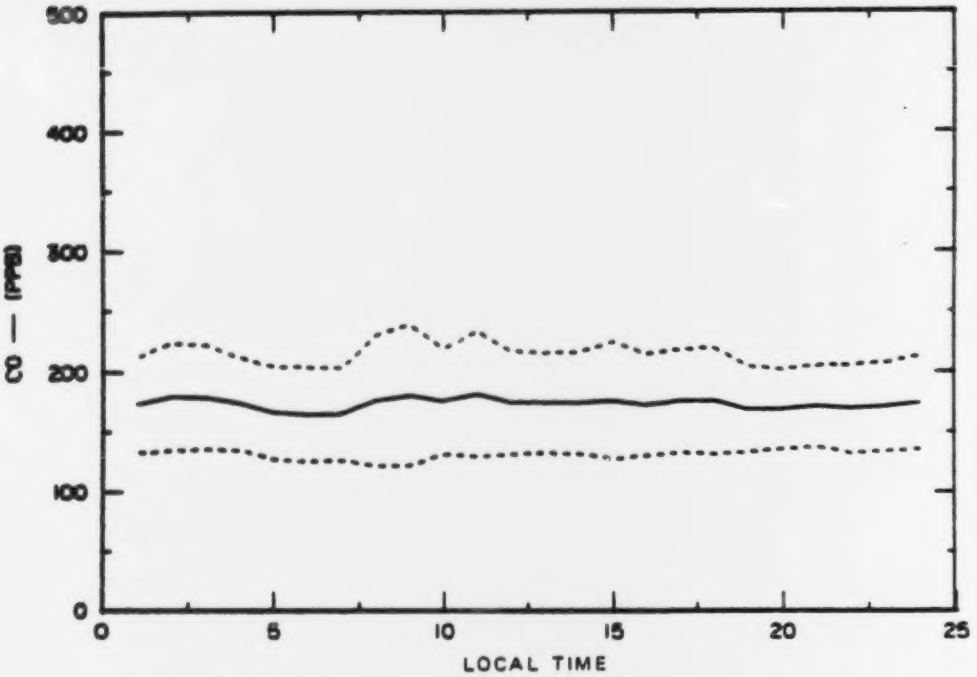

FIGURE 50 MEAN DIURNAL VARIATION IN CO AT JETMORE, KANSAS, 3 APRIL-20 MAY 1978

175 (± 40) ppb is typical of background levels at this latitude. It is also clear from Figure 50 that no diurnal variation exists, which is another indication of the lack of impact from urban sources.

An analysis of light HC data suggests that the C_3 to C_5 alkanes and CO levels are typical of clean rural environments. Fluorocarbon-12 (F-12) is an ideal indicator of any urban source of contamination, since it is completely inert and almost exclusively emitted in urban areas. The overall average concentration of about 240 ppt (Table 21) is almost identical to the prevailing geophysical background of F-12. In addition, the variability of F-12 was found to be small (about 5 percent). These observations support the view that there is no significant urban-type contamination above the background levels in the region of operation.

A third indicator of local photochemistry is PAN. The concentration of PAN was found to be very low and did not exceed 1 ppb. On nearly 75 percent of the days, the mean PAN concentration level was less than 0.5 ppb. The daily average PAN concentration was never less than 0.1 ppb. As we shall see later, the very low PAN concentration is consistent with the precursor mix present in this area.

1. Ozone-NO_x Measurements

Figure 51 shows the variation of maximum 1-hour daily O_3 and the daily O_3 average during the study period (3 April to 20 May). It is clear from Figure 51 that the maximum one-hour O_3 never exceeded 70 ppb, while the daily mean never exceeded 55 ppb. Figure 52 shows the average

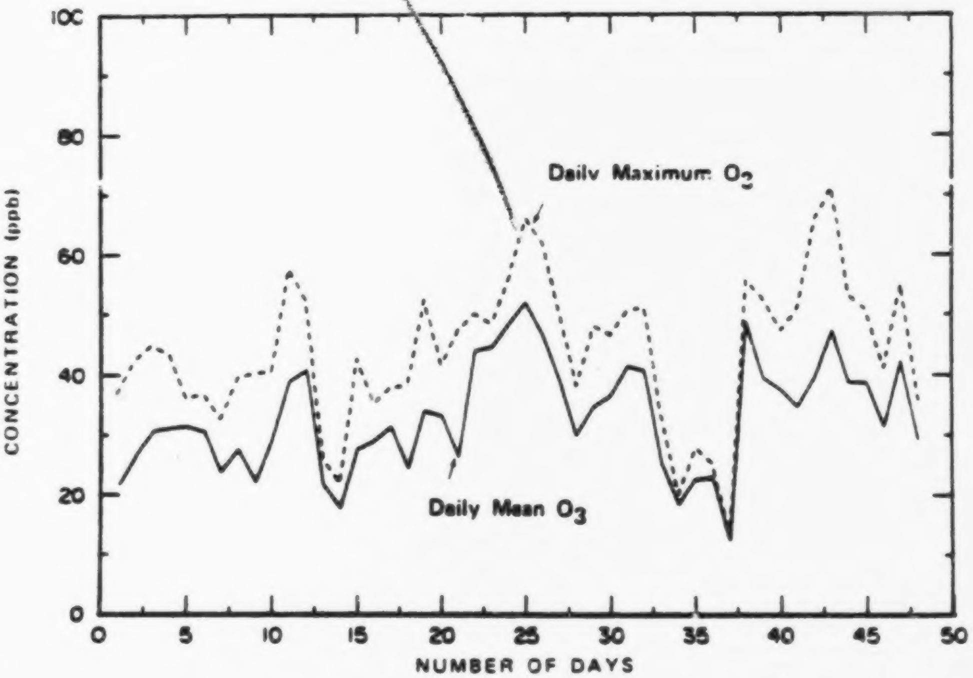

FIGURE 51 MEAN AND MAXIMUM O_3 AT JETMORE, KANSAS, 3 APRIL-20 MAY 1978

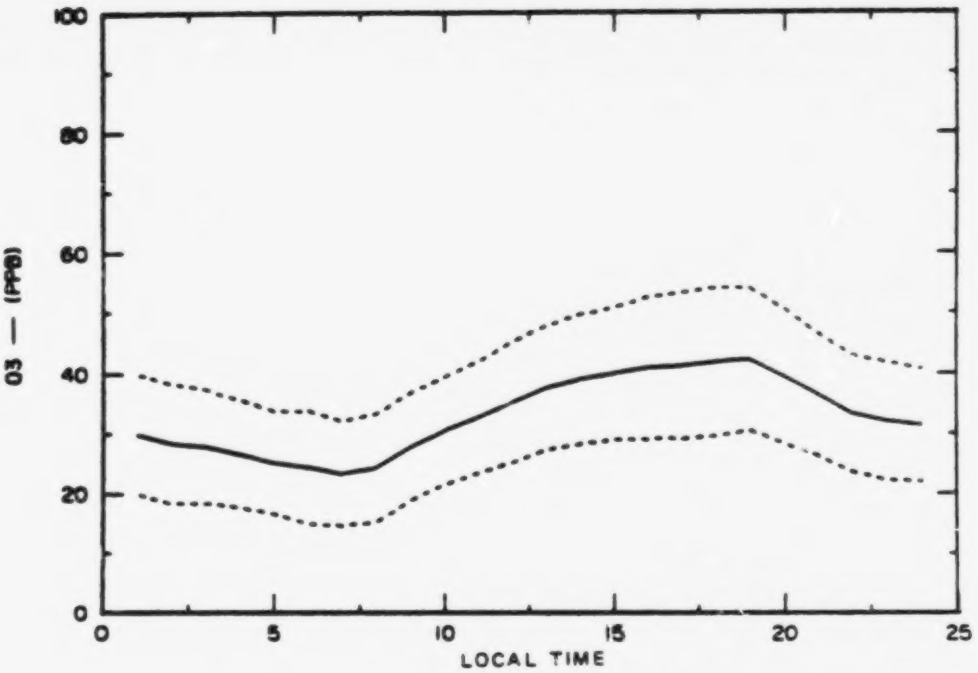

FIGURE 52 MEAN DIURNAL VARIATION IN O_3 AT JETMORE, KANSAS, 3 APRIL-20 MAY 1978

diurnal variation of O_3 and the standard deviation associated with this diurnal variation. It is apparent that the O_3 maximum appears somewhat late (1600-1800 LT).

Figures 53 to 55 show the mean diurnal variation of NO, NO_2, and NO_x. Average levels of NO, NO_2, and NO_x are 1.2 ppb, 4.3 ppb, and 5.5 ppb, respectively. The NO/NO_x ratio of 0.22 is comparable to that observed at some rural sites in the SURE data (cf. Table 15). Although the mean NO levels throughout the day are essentially constant, NO_2 shows a slight decline in the afternoon. The sensitivity of NO and NO_x measurements was better than 1 ppb; therefore, these data should be reliable. The source of the NO_x in this region is currently unclear. Agricultural sources of NO_x cannot be ruled out and should be further studied.

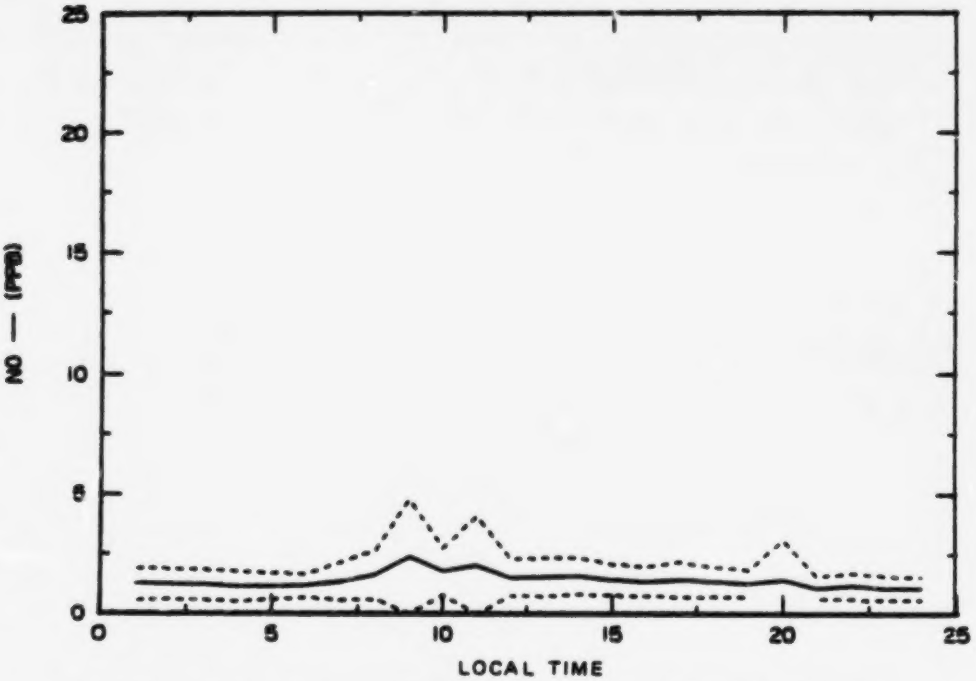

FIGURE 53 MEAN DIURNAL VARIATION IN NO AT JETMORE, KANSAS, 3 APRIL-20 MAY 1978

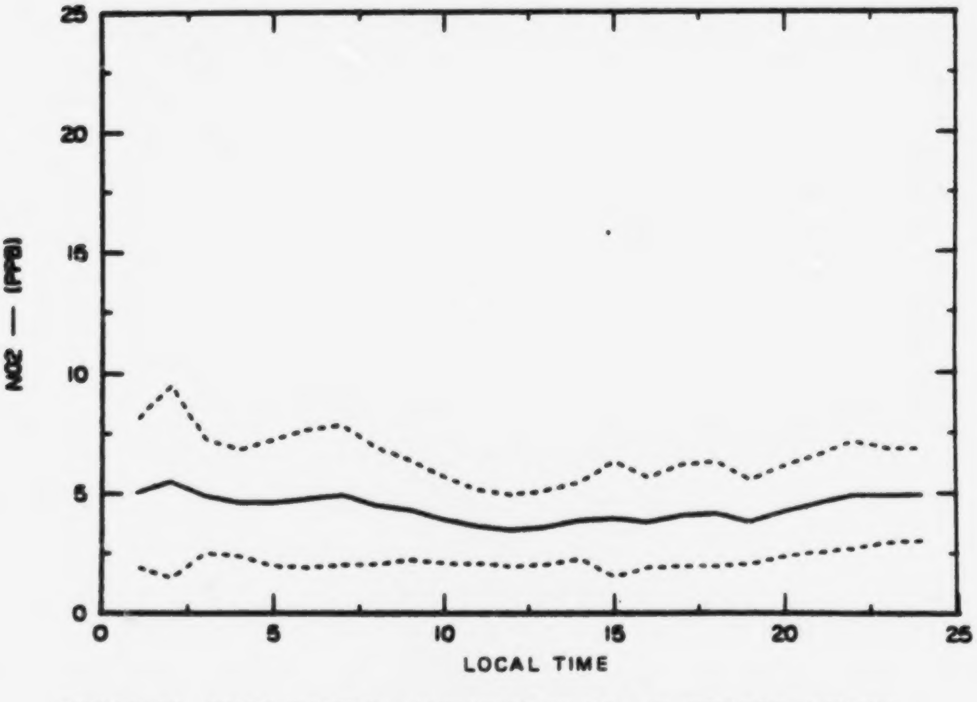

FIGURE 54 MEAN DIURNAL VARIATION IN NO_2 AT JETMORE, KANSAS 3 APRIL-20 MAY 1978

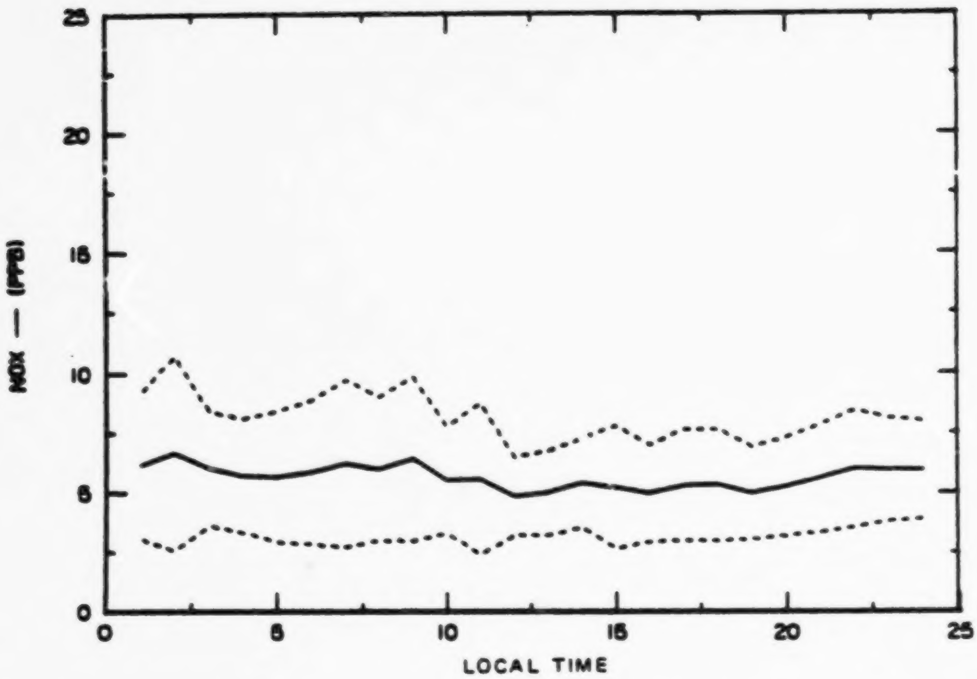

FIGURE 55 MEAN DIURNAL VARIATION IN NO_x AT JETMORE, KANSAS, 3 APRIL-20 MAY 1978

Both hydrocarbons and NO_x are present at relatively low concentrations at this site. Excluding the essentially unreactive CH_4 and C_2H_6, there are only about 30 ppbC of alkanes and 1.6 ppbC of alkanes. These low levels of HCs seem to be consistent with the very low levels of PAN at this location. It should also be added that aircraft data taken in the vicinity of Jetmore showed O_3 levels aloft comparable to or larger than the hourly maximum observed at ground level. Therefore, while O_3 undergoes a diurnal variation at ground level, we feel it is largely dictated by O_3 loss at the ground and mixing from aloft. Not only are the HCs here largely slow reactive (alkanes), but they are also present in low concentrations. A small amount of local O_3 production, however, cannot be ruled out.

The days where the one-hour O_3 maximum was found to be in excess of 58 ppb were studied. Figures 56 to 58 display the O_3, CO, CH_4 and NO_x data for these days, together with the wind speed data. Figure 57 shows somewhat higher than average CO levels in the morning that rapidly decline in the afternoon. The decline in CO and NO_x is associated with an increase in O_3. This is indicative of mixing processes that are

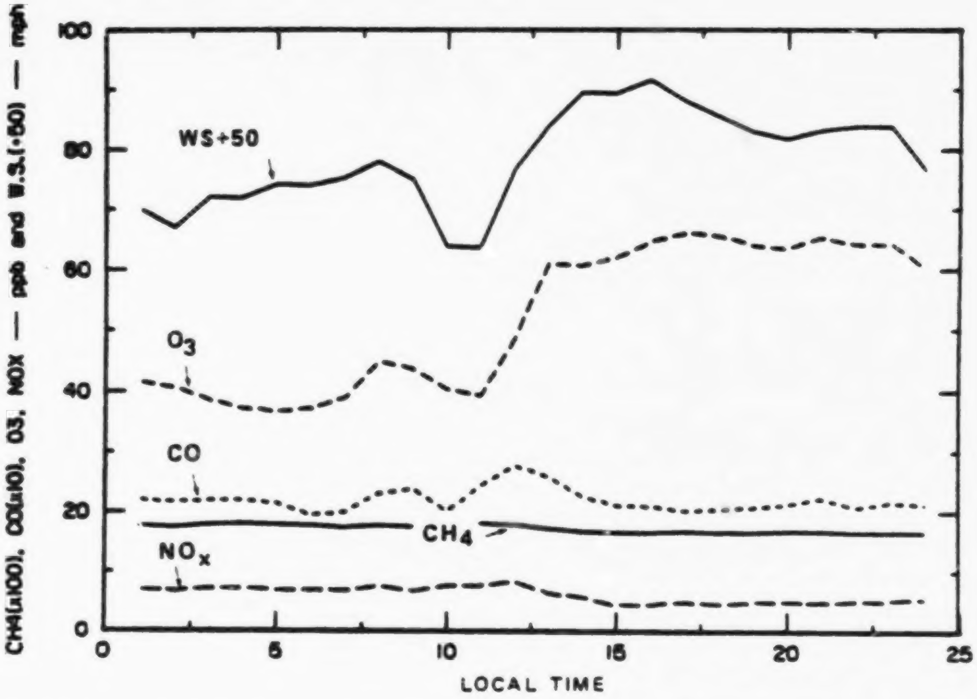

FIGURE 56 MEAN DIURNAL VARIATIONS IN WIND SPEED AND SELECTED POLLUTANTS AT JETMORE, KANSAS, ON 27 APRIL 1978

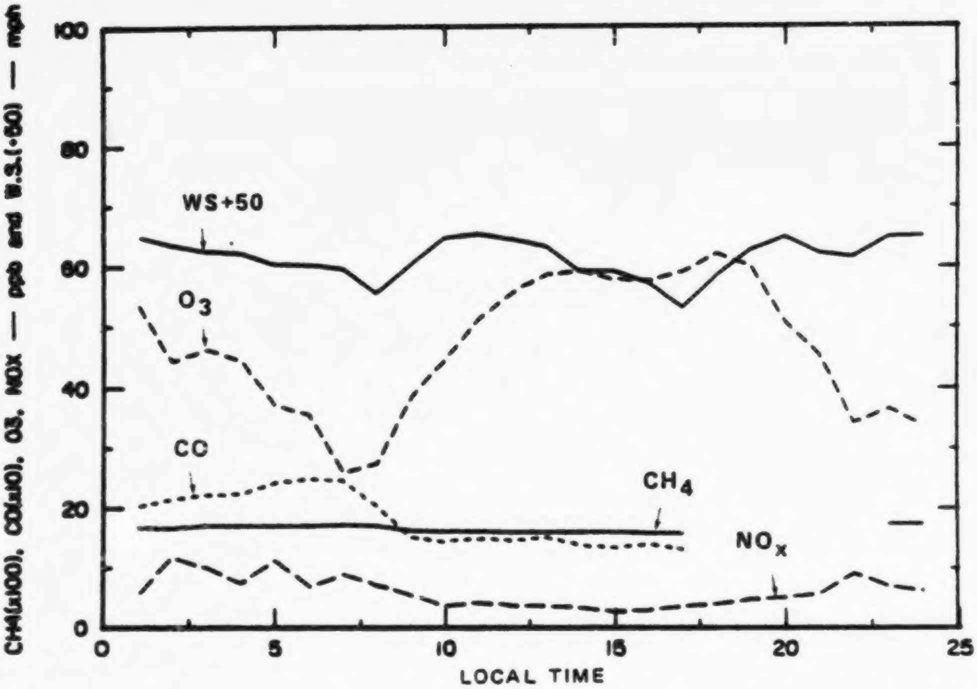

FIGURE 57 DIURNAL VARIATIONS IN WIND SPEED AND SELECTED POLLUTANTS AT JETMORE, KANSAS, ON 28 APRIL 1978

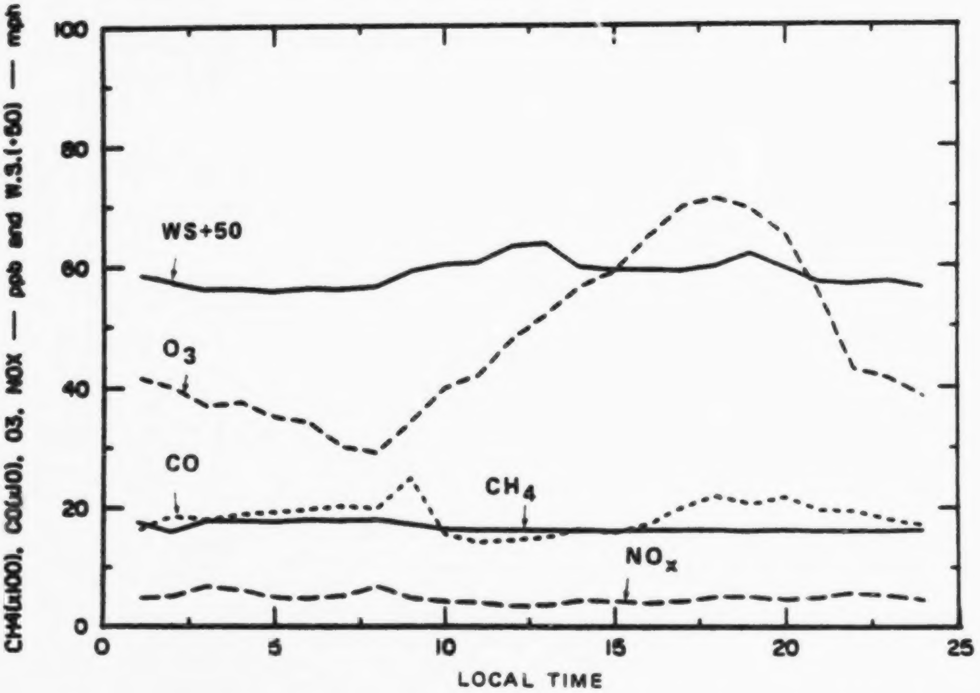

FIGURE 58 DIURNAL VARIATIONS IN WIND SPEED AND SELECTED POLLUTANTS AT JETMORE, KANSAS, ON 15 MAY 1978

replenishing O_3 in the boundary layer from aloft. On 27 April (Figure 56), the CO levels are high throughout the day and may indicate some contamination. The wind speed in the afternoon was high (> 30 mph); therefore, the O_3 maximum, once achieved, was maintained by constant mixing from aloft.

The CO levels on 15 May were somewhat higher, but are within the range of variability of clean continental background of CO. The wind speed was less than 10 mph. It is possible that some O_3 transport may have occurred.

Thus, it appears that this location is probably deficient in HCs and that little photochemical activity is going on. The O_3 is largely brought down to the ground from the free tropospheric reservoir.

2. O_3 and ^{7}Be Relationship

Since the O_3 at Jetmore did not appear to be photochemically generated, we tested the data to see whether a correlation between O_3 and ^{7}Be existed. The ^{7}Be data were averaged over 24 hours, and these were compared with daily average O_3. Figure 59 shows the daily average concentrations of O_3 and ^{7}Be at Jetmore. Typically, average ^{7}Be concentrations varied between 80 and 400 pci/1000 SCM. In one instance, levels as high as 640 pci/1000 SCM were measured. It is clear from Figure 59 that fairly large variations in ^{7}Be levels occur. It also appears that peaks in O_3 coincide with corresponding peaks in ^{7}Be, at least some of the time. Figure 60 shows a scatter diagram of O_3 versus ^{7}Be. As indicated by the scatter in the data, the linear correlation was very low ($R = 0.25$). The daily one-hour O_3 maximum is more representative of free tropospheric O_3, and it was tested to see whether any correlation existed with daily average ^{7}Be. This, too, failed to show a substantial correlation although a small improvement ($R = 0.31$) was observed. When we considered only those days when ^{7}Be concentration was greater than

300 pci/100 SCM, this correlation showed significant improvement (R = 0.29).

3. Conclusions

It appears that a location such as the Jetmore, Kansas, site is low in hydrocarbons abundance, and even the HCs present are alkanes which react slowly compared to alkenes. The NMHC (less C_2H_6) was present at a concentration of 30 ppbC along with an alkene concentration of less than

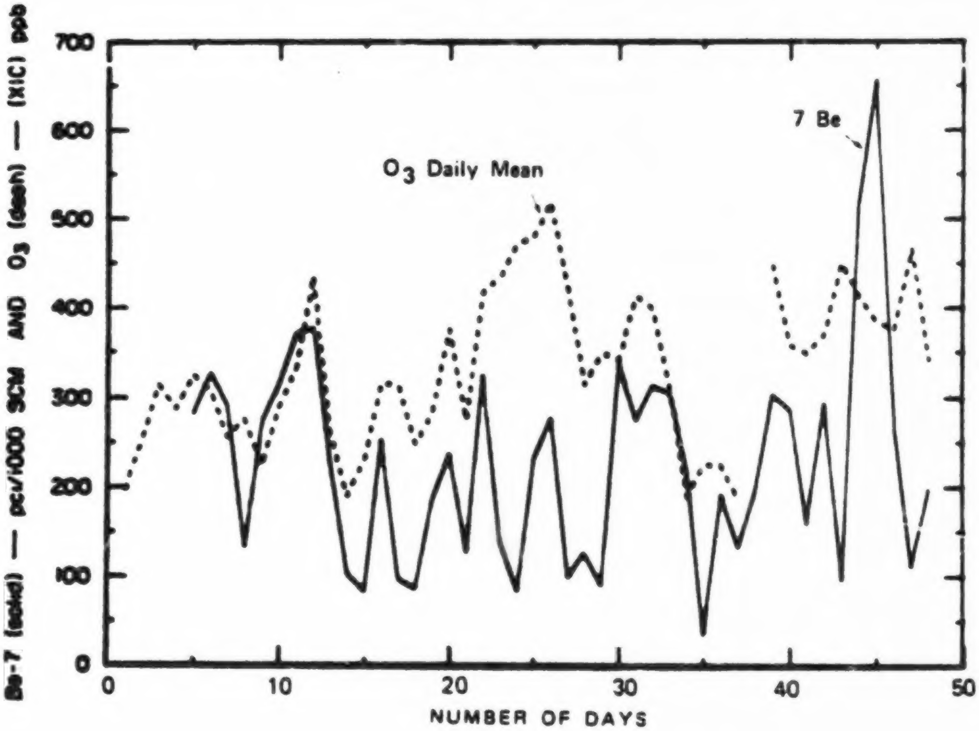

FIGURE 59 MEAN DAILY O_3 AND ^7Be AT JETMORE, KANSAS, 3 APRIL-20 MAY 1978

Ozone mean obtained for interval 1700-1700.

2 ppbC and an NO_x concentration of 5 ppbC. It does not appear that local photochemical activity that could result in significant O_3 formation was occurring. The indications are that O_3 concentration was largely controlled by mixing from the free troposphere and ground level destruction.

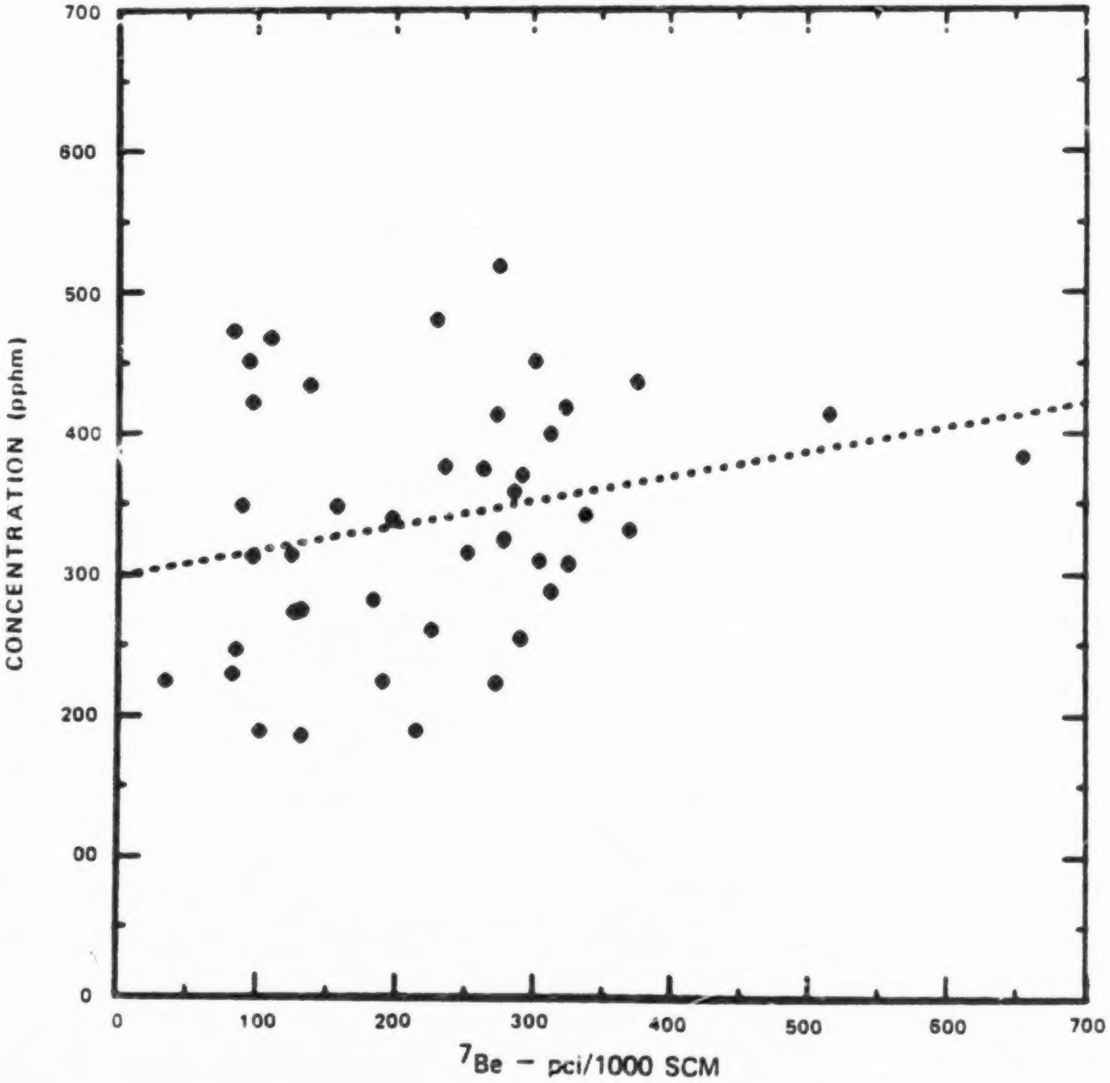

FIGURE 60 SCATTER DIAGRAM FOR MEAN DAILY O_3 VERSUS ^{7}Be AT JETMORE, KANSAS, 3 APRIL–20 MAY 1978

VI CONCLUSIONS

A primary objective of this investigation was to survey and summarize the current state of knowledge about nonurban NO_x/O_3 interactions. Our results show that present knowledge can be characterized as fragmentary. Consequently, there is currently no direct quantitative evidence that answers the question that motivated this study, namely, whether increases in urban NO_x emissions will enhance, reduce, or have no effect on nonurban ozone. Relevant previous research efforts have not been aimed at this specific problem and the inferences that can be drawn from them are at best qualitative and suggestive, rather than quantitative and conclusive. Therefore, additional research is needed to establish the relationship between NO_x and nonurban ozone. Pursuant to another objective of the project, three research programs are proposed in Section VII that respond to this need. The available evidence allows some tentative conclusions to be reached nonetheless, and these are discussed below.

NO_x transported from urban to nonurban areas affects ozone formation by participating in two categories of chemical processes: local and nonlocal. In the local domain, transported NO_x increases the nonurban NO_x level, and thus participates in the local chemical reactions that form ozone. In a nonlocal mode, NO_x and hydrocarbons of urban origin react to form ozone in an air mass on the way to a nonurban area. Ozone thus arrives ready-made, and combines with existing ozone to increase the concentration at the nonurban locale. The time of occurrence differs for these two effects. Local chemical effects tend to predominate in the morning, which implies that transported NO_x must arrive during the night or early in the morning in order to participate in the local photochemical process. Nonlocal effects require several hours to develop, since the air mass must travel distances of the order of tens of miles from source to receptor. Consequently, enhanced levels of nonurban ozone due to nonlocal causes tend to occur in the late afternoon and early evening, and sometimes at night.

We consider the following two issues to be important:

- Which effect, local or nonlocal, is most frequently associated with high nonurban ozone?
- What is the likely impact of nonurban ozone if NO_x levels increase either in a local or nonlocal mode?

Regarding the first question, the analysis of field data collected in the SURE (see Section IV) indicates that nonlocal effects predominated when ozone levels exceeding 100 ppb occurred in rural and suburban areas. Of the nine SURE sites investigated, those exhibiting at least one hour when ozone exceeded 100 ppb included all four rural sites (Sites 1, 4, 6, and 9) and one suburban location (Site 8). Site 8 is influenced by emissions of ozone precursors from commuter traffic, but is also surrounded by several medium-sized cities. Hence, it is also a receptor for pollutants that originate in these urban centers. The four rural sites, by contrast, show no influence from traffic or other specific sources.

Ozone exceeded 100 ppb on 16 days at these five sites. Nonlocal effects are the probable cause of the high ozone on 11 days, and both local and nonlocal factors are evident on the remaining 5 days. It is apparent, therefore, that nonlocal effects are closely associated with all the high ozone events at the SURE sites. While it is risky to generalize based on this small sample, the evidence does suggest that ozone formation in an air mass en route to a nonurban site is the principal mechanism that leads to high ozone levels, and that ozone synthesized from local precursors (which may be affected by transported NO_x and hydrocarbons) plays a lesser role. In particular, it appears that locally formed nonurban ozone does not by itself lead to concentrations exceeding 100 ppb, although the local component of the total ozone burden can be substantial depending on time of day. The analysis further suggests that transport times of the order of six to eight hours are most likely to be associated with the observed high ozone.

As noted earlier, it is not possible to answer confidently the question about the likely impact of increased NO_x on nonurban ozone. The review of the literature reveals a convergence of several independent lines of research that suggest that the likely impact of increases in NO_x emissions will be to enhance nonurban ozone. This judgment agrees with the consensus response to a question on NO_x control strategies contained in the survey of expert opinion (see Section III-B-4). However, this estimate of likely impact is only qualitative, and cannot serve as a basis for regulatory decisions. Moreover, the impact of NO_x on nonurban ozone is undoubtedly a function of geographical location since ozone production can be NO_x-limited at some sites, but not at others. An example of the latter is the site in Jetmore, Kansas (see Section V), where local ozone production appears to be limited by hydrocarbons, rather than by NO_x. Hence, it is inappropriate to attempt to state a general rule that applies equally to all locations. Nevertheless, although the signs are uncertain, they seem to point in the direction of deleterious effects, adding a note of urgency to the need to perform more research to test the validity of these preliminary indications.

If confirmed by more detailed studies, the conclusions discussed above imply that more stringent NO_x controls may be necessary to alleviate (or at least not worsen) the problem of high ozone levels at some nonurban areas. Because of the geographically widespread nature of the problem, control strategies with a regional scope should be the preferred approach to a solution. However, the indications are that not all nonurban areas would benefit from such measures, and that it would be more efficient to tailor controls to specific areas.

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VII RECOMMENDATIONS FOR FURTHER RESEARCH

The previous discussions have made it clear that additional study is needed to characterize quantitatively (and perhaps mechanistically) the relationship between NO_x and O_3 in nonurban areas. This can best be done in the context of a program specifically designed for this purpose. Three such programs are outlined below. Two are retrospective analyses of existing data that would be relatively easily performed, whereas the third program entails data collection as well as analysis. These studies are intended to determine the role NO_x has played in oxidant formation in the recent past, and to define the impact of future changes in NO_x on the formation of nonurban ozone.

A. Study I: Analysis of Data from Rural Locations

In many rural locations (as distinct from remote locations), the NO_x levels vary from 5- to 50-ppb levels. The reliability of data collected in this concentration range is fair to good. Over the last five years, a number of stations have been operated to collect both short- and long-term NO_x data on an essentially continuous basis. (The short-term implies a period of one to three months, while the long term could be three months to several years.) We have in the past looked at a limited amount of long-term NO_x data (Singh et al., 1977) and are assured of the availability of much more extensive data bases around the country.

Because of less stringent controls on the emissions of NO_x compared to HC emissions, the amount of NO_x released to the atmosphere has steadily increased over the past five years. We suggest that a comprehensive analysis of NO_x and O_3 data in rural locations within the United States be conducted with the primary view of obtaining answers to the following questions

- Has the atmospheric abundance of NO_x increased over the last five years?
- Is this increase (if any) consistent with regional increases in NO_x emissions?
- Have the corresponding O_3 levels registered any changes? If so, what kind of changes?
- Are the O_3 variabilities in any way, statistically or mechanistically, related to the variabilities of NO_x? If so, what is the nature of this relationship?

It is not our intent here to develop a detailed plan for such a study; rather, we are attempting to outline the nature of analysis that would utilize existing data, obtained at great cost, to study NO_x/O_3 relationships under actual atmospheric conditions. The effort to conduct such a study should be a small one (six to eight months) and the potential utility of results would more than justify the cost.

B. Study II: Analysis of Data from the Los Angeles Area

This program would yield direct evidence about the kind of downwind impact that can be expected when urban NO_x emissions increase. The program entails a retrospective analysis of air-quality data collected in the 1960s in areas downwind of the Los Angeles basin. It is well known that NO_x emissions from automobiles increased substantially in Los Angeles in the late 1960s. The increases in NO_x resulted from attempts to control automobile hydrocarbon emissions. At the time, the technological solution for controlling hydrocarbons consisted of adjusting the gasoline/air mixture for more complete combustion; the desired reduction in hydrocarbon emissions was achieved at the expense of increased NO_x. The situation was corrected in the early 1970s, when limits were placed on emissions of both hydrocarbons and NO_x. Thus, in the late 1960s, the Los Angeles area experienced precisely the condition that concerns the present study, namely, increased NO_x and reduced hydrocarbons. An analysis of the air quality and meteorological data before and during the time of increased NO_x would answer the question: What happens to ozone downwind of an urban area when NO_x increased and hydrocarbons decrease?

The method of "intervention analysis" developed by Box and Tiao (1975) would be especially useful for performing the suggested study. In fact, the method has been applied to the problem of determining the impact of the aforementioned engine adjustments on ozone levels in downtown Los Angeles (Tiao et al., 1975). However, the impact on ozone at downwind locations was not examined.

Effects of increased NO_x emission on NO concentrations at various sites in Los Angeles were recently examined by Phadke et al. (1978), while Trijonis (1978) analyzed long-term trends in NO_2. Neither of these studies addresses the issue that concerns us here, since they are restricted to NO and NO_2, and no attempt was made to examine the interactions between NO_x and O_3.

C. Study III: Data Collection and Analysis Program

One of the major uncertainties in assessing the role of NO_x in rural locations is simply the lack of available information on which to base such as assessment. No models exist that are adequately validated for rural environments. Besides, there is no reason to believe that most rural areas would have identical NO_x/O_3 relationships; on the contrary, the precursor compositions in various rural locations may result in completely different NO_x/O_3 relationships.

Recognizing that we are in the preliminary stages of defining the rural NO_x/O_3 relationships, we present here a field program that would provide a great deal of useful information about these relationships, and would lay the groundwork for more extensive field studies in the future, should they be needed. The proposed field program would provide an essential insight into the NO_x/O_3 relationships in several rural locations. The basic field program can be outlined as follows:

- Select five to ten representative rural sites in the country. These should include rural sites downwind of large and small urban centers of varying characteristics, downwind of power plant plumes, refineries, isolated rural centers, and the like.

- Equip a mobile environmental laboratory with reliable O_3, NO_x and HC instrumentation. Here we would expect that NO_x analysis sensitivity be about 1 ppb.
- Go to Site 1 (say in July) with the mobile laboratory and a dozen Teflon bags of 500-liter volume each. On a given day, fill five bags simultaneously between 0600 and 0900 LT. Analyze them for HC distributions, O_3 and NO_x.
- Spike four bags with NO_x levels of 2 NO_x, 3 NO_x, 5 NO_x, and 10 NO_x, where 1 NO_x would be the NO_x concentration in the unspiked bag.
- Monitor these bags for HCs, NO_x, and O_3 for the next 36 hours.
- Quantify and collect air quality and meteorological information (e.g., solar flux).
- Repeat above experiments on another day.

It is expected that normal scientific procedures (e.g., conduct replicate experiments) be used to ensure reliability. The above steps could then be repeated at other sites.

A five-site experiment of this type could be conducted over a five to eight week period with minimal cost. It should be added that the spiking principle is well known and has been used in the past to obtain valuable information. However, the bags used have been too small, and no attempt at a systematic characterization of NO_x/O_3 dependence has been made to date. The suggested systematic approach would be relatively inexpensive, and would yield useful information about NO_x/O_3 relationships. For example, the program would provide data that would answer the question of whether NO_x/O_3 relationships at various representative rural locations are similar or different. In addition, the potential impact of changes in NO_x levels would be demonstrated. Such a field program would benefit from the simplicity of the smog chamber approach and the realism of field conditions.

D. Additional Topics for Investigation

The following emerged in the course of the study as important topics that require further research to characterize NO_x/O_3 interactions in the nonurban atmosphere.

- Estimate the tropospheric half-life of NO_x.
- Establish the role of low-reactive and natural hydrocarbons in nonurban ozone formation.
- Define the significance of organic nitrates as reservoirs of NO_x and organic radicals.
- Establish the identity and relative importance of sinks and natural sources of NO_x.

The first item is important in estimating the time (and consequently distance) during which NO_x can be transported in significant quantities. Thus, a short half-life would limit the zone of influence of an urban source and vice versa. To be sure, a number of the studies reviewed, and the expert commentary, suggest that the half-life is of the order of 24 hours. However, many uncertainties remain. Thus, the question of sinks and sources of NO_x in the nonurban environment is one that must be resolved as part of the process of estimating the half-life of NO_x. Data needs related to the issue of the half-life of NO_x include nighttime measurements of NO_x aloft. Preferably, these should be performed in a Lagrangian mode. Also required are highly sensitive measurements of levels NO_x as low as 0.10 ppb.

The zone of influence of urban areas can be expanded if longer-lived organic nitrates were to act as reservoirs of NO_x and organic radicals. Current knowledge about this topic is sketchy and somewhat speculative. To resolve this question, we need to obtain accurate measurements of organic nitrates, expecially PAN, in nonurban areas. From such data it may be possible to estimate the quantity of NO_x contributed by this source.

No assessment of the role of NO_x in ozone formation can be complete without considering the third dimension, namely, the hydrocarbons. To do so, we need to obtain more detailed hydrocarbon measurements at rural sites, including aldehydes and natural hydrocarbons. The discussions in Sections II and III make it apparent that the role of natural hydrocarbons is currently the subject of considerable controversy; more data are needed to settle the argument.

Investigation of these topics would require new data to be gathered and analyzed. Such investigations could be pursued independently of the three projects outlined above.

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16. ABSTRACT

This study surveys and summarizes current knowledge about the role of oxides of nitrogen (NO_x) in the formation of ozone (O_3) in nonurban areas. Project elements include a literature review, a survey of expert opinion, and analyses of field data.

The results of the study show that present knowledge about NO_x/O_3 interactions in nonurban areas is fragmentary, and that there is no direct quantitative description of the link between urban NO_x and nonurban O_3.

A preliminary analysis of nine rural and suburban sites indicates that transport is the principle mechanism associated with ozone levels that exceed 100 ppb. The analysis further suggests that transport times of the order of six to eight hours are most likely to be associated with the high ozone observed at these sites.

17. KEY WORDS AND DOCUMENT ANALYSIS

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